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UNIVERSITY OF ALBERTA

CHEMICAL AND SENSORY EVALUATION OF TASTE AND ODOUR IN RAW AND TREATED WATER

BY

© DAVID W. RECTOR

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES AND

RESEARCH IN PARTIAL FULFILLMENT OF THE REQUIREMENTS

FOR THE DEGREE OF MASTER OF SCIENCE

IN

ENVIRONMENTAL SCIENCE

DEPARTMENT OF CIVIL ENGINEERING

EDMONTON, ALBERTA

FALL 1994

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The undersigned certify that they have read, and recommend to the faculty of Graduate Studies and Research for acceptance, a thesis entitled CHEMICAL AND SENSORY EVALUATION OF TASTE AND ODOUR COMPOUNDS IN RAW AND TREATED WATER submitted by DAVID W. RECTOR in partial fulfillment for the requirements for the degree of MASTER OF SCIENCE in ENVIRONMENTAL SCIENCE.

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This thesis is dedicated to Christine whose support, encouragement and love made this thesis possible.

Abstract

Taste and odour in finished drinking water supplies is often regarded as an aesthetic problem but it can cause consumers to question the safety of their water supply and it may make the water unacceptable to consumers. As a result, they may seek alternative sources of supply such as bottled water or point-of-use devices which may expose them to water of questionable microbiological or chemical quality. For most water utilities, avoiding customer complaints is a major priority. However, identifying the causes of odour is frequently difficult because of the very low concentrations of some contaminants that can cause taste and odour problems. The study reported herein investigated the sensory and chemical characteristics of the raw and treated water supply for the City of Edmonton during a spring taste and odour event.

Granular Activated Carbon, preloaded with raw and treated water (with and without Powdered Activated Carbon), was sequentially Soxhlet extracted with three solvents: hexane, dichloromethane and ethyl acetate. The resulting extracts were reduced and subjected to gas chromatographic (GC) analysis with three flame detectors: ionization detection, a human sensor and mass selective detection. After identifying the retention times of the odorous components, attempts were made to isolate and concentrate these fractions by preparative gas chromatography for further analysis. These attempts at concentrating these odorous contaminants were largely unsuccessful as a result of the low or zero recoveries obtained.

The spring odour character of the North Saskatchewan River was found to be very complex. Contributing odour agents were geosmin, 2-methylisoborneol, other terpenoid compounds, aldehydes and sulfur containing compounds.

GC sniffing analysis was shown to be highly effective in detecting the odorous components of the raw and treated water as the human sensor selectively discriminates between those compounds present at high concentrations with high odour concentrations and those compounds present at low concentrations with low odour threshold concentrations. The results of the sniffing analysis were used to focus the analytical efforts on those portions of the complex gas chromatogram which provided distinctive and strong odours.

GC Sniffing analysis also demonstrated that Granular Activated Carbon was not an appropriate adsorbent to concentrate taste and odour compounds given the incremental desorption of the identified taste and odour compounds geosmin and 2-methylisoborneol with three successive solvents. Additionally, the procedure to remove the adsorbed material (Soxhlet extraction and Kuderna Danish evaporation) was found to be very harsh and prone to losses of odour compounds due to their volatility or decomposition. This was especially true for some of the more thermally labile sulfur compounds known to cause taste and odour problems in other jurisdictions.

The results of the odourgrams showed that there is little difference in the odour characteristics of the raw water and the pilot plant process stream that did not use powdered activated carbon during the spring taste and odour event of 1989. The powdered activated carbon was effective in removing the odours caused by 2-methylisoborneol and the tentatively identified 2-isopropyl-3-methoxypyrazine. The powdered activated carbon was less effective in removing the odour caused by geosmin. The results demonstrated the requirement and utility of applying powdered activated carbon during taste and odour events in Edmonton.

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The bulk of the mass spectral analyses in this thesis were performed on a gas chromatography-mass selective detector which was obtained through funding provided by the Natural Sciences and Engineering Research Council.

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List of Abbreviations

AC	Activated Carbon
APHA	American Public Health Association
AWWA	American Water Works Association
AWWARF	American Water Works Association Research Foundation
CLLE	Continuous liquid liquid extraction
ClO_2	Chlorine dioxide
CLSA	Closed loop stripping apparatus
DCM	Dichloromethane
dd	Defies description (see odourgrams)
DOC	Dissolved organic carbon
EICP	Extracted ion current profile
FPA	Flavour profile analysis
GAC	Granular activated carbon
GC	Gas chromatograph
GC-ECD	Gas chromatograph electron capture detection
GC-FID	Gas chromatograph flame ionization detection
GC-MSD	Gas chromatograph mass selective detection
GC-Sniff	Gas chromatograph human sensory detection
H_2O_2	Hydrogen peroxide
HPLC	High performance liquid chromatography
IBMP	2-Isobutyl-3-methoxy pyrazine
ID	Internal diameter
IPMP	2-Isopropyl-3-methoxy pyrazine
L	Litre
LLE	Liquid-liquid extraction
MW	Molecular weight
MIB	2-Methylisoborneol
mg/L	Milligrams per litre (ppm)
NTU	Nephelometric turbidity units
ng/L	Nanograms per litre (ppt)
NH_2Cl	Monochloramine
NSR	North Saskatchewan River
OII	Odour intensity index
OLSA	Open loop stripping apparatus

OTC	Odour threshold concentration
PAC	Powdered activated carbon
PAH	Polycyclic aromatic hydrocarbons
PCB	Polychlorinated biphenyl
PFBOA	Pentafluorobenzylhydroxylamine (aldehyde derivatizing agent)
POG	Perceptio-olfactograms
ppb	Parts per billion (µg/L)
ppm	Parts per million (mg/L)
ppt	Parts per trillion (ng/L)
PTFE	Polytetrafluoroethylene
RT	Retention time
SIM	Selected ion monitoring
TCU	True colour units
TLV-STEL	Threshold limit value - short term exposure level
TLV-TWA	Threshold limit value - time weighted average
TOC	Total organic carbon
TON	Threshold odour number
µg/L	Micrograms per litre (ppb)
UV	Ultraviolet
WEF	Water Environment Federation
WHO	World Health Organization
XAD	Series of synthetic resins produced by Rhom and Haas

1.0 Introduction

1.1 Significance of Taste and Odour to Consumer Acceptance

Increased environmental awareness among the public has enhanced their concern about potential hazards associated with trace levels of certain chemicals and elements in drinking water. Taste and odours in potable water supplies are caused by specific chemicals of natural and anthropogenic origin. Consumers are able to detect the presence of these substances by means of their senses and they logically presume that the presence of undesirable substances in their drinking water may be associated with a health risk (Mallevialle and Suffet 1987). Because humans have evolved over time to use their senses to warn them of food that has been spoiled, this is not an unreasonable assumption. However, the ability of consumers to detect substances with their senses may lead them to conclusions that contradict the greatest health risks. Hansson et al. (1987) illustrated this point in Australia where they had difficulty maintaining a free chlorine residual in their distribution system such that they had no odour, but did have 3 cases of amoebic meningitis, a normally fatal illness. They were able to isolate the disease-causing amoeba in the distribution system. When they switched to chloramines as a final disinfectant for more effective amoeba control, they received numerous complaints over the taste and odour caused by the chloramines.

Hoehn (1988) cited an American Water Works Association (AWWA) survey where 30% of the population described bad tastes in their water. de Greef et al. (1983) showed that over 37% of the 3073 persons surveyed in the Netherlands described the water as having a taste or odour. An AWWA Research Foundation study (Manwaring et al. 1986), found that 20% of the surveyed population used bottled water or a point-of-use device because they were dissatisfied with the taste or odour of their tap water. Clearly, taste and odour is extremely important to consumer acceptance of a potable water supply. In a broader sense, reference to the World Health Organization (WHO) definition of health as a state of complete physical, mental and social well being, and not merely the absence of disease or infirmity, suggests that off-flavours in drinking water may constitute a health problem (Zoeteman et al. 1980). The presence of taste and odours may cause enough concern that a consumer feels compelled to utilize alternative means of providing drinking

water such as bottled water or a point-of-use device. These alternate sources may be of questionable microbiological and chemical quality (U.S. GAO 1991, Consumer Reports 1990). Zoeteman (1980) has shown that consumers will also substantially reduce their consumption of tap water (by 43% in their survey) if there is an off-flavour present in the potable water supply. Because consumers understandably question the safety of water when it has an off-flavour, and they do not have the means to perform their own analyses, a fundamental measure of the quality and acceptability of drinking water is its organoleptic quality (i.e. taste and odour).

WHO (1981) stated that the taste and odour of drinking water should not be objectionable to 90% of the population. Zoeteman et al. (1972) suggested that the limit should be higher with 95% of the population finding the water not objectionable. This can be difficult as Amoore (1986) has shown that the perceived threshold odour by a group of 205 people exhibited a normal Gaussian distribution with 96% of the population falling within two standard deviations of the mean. This range spans from 1/16th to 16 times the median Odour Threshold Concentration (OTC). This is the reason why a few very sensitive customers can detect and complain about an off odour while most people may be unaware of any problem.

Cees et al. (1974) demonstrated this phenomenon in their studies of 4 chemicals (including geosmin) and a panel of 120 individuals. They noted that odour sensitivity can vary by a factor of 10,000 for various chemicals. As shown in Table 1.1, 4.4% of the population could still detect an odour at 1/100th the reported OTC. With a service population of approximately 800,000, this would mean that 35,000 consumers in Edmonton would be able to detect, and more importantly complain, of an off-odour in the finished water at 1/100th the reported OTC for a taste and odour producing chemical. Consequently, compounds cannot be dismissed as taste and odour causative agents should their concentrations fall, even significantly, below their reported OTC's.

Table 1.1 Relationship Between OTC and Percentage of Observers Detecting Odour (after Cees et al. 1974)

Concentration	% of Population Still Capable of Detecting an Odour
OTC	50
0.1 x OTC	15
0.03 x OTC	7.8
0.01 x OTC	4.4

Individual odour sensitivity maximizes at approximately 20 years of age and decreases by half for every 22 years after that. Contrary to popular belief, women are not more sensitive than men and non-smokers are not more sensitive than smokers (Amoore 1986). Some individuals exhibit specific anosmia, or smell blindness, to certain chemicals. As an example, 36% of the population were found to be anosmic to isobutyraldehyde (Amoore 1986). Maga (1987) found that some odours are inoffensive in a medium where they are expected but the same odour can be offensive when it occurs in a medium where it is not expected (e.g. drinking water). For example, the distinctive musty odour of potatoes is due, in part, to 2-isopropyl-3-methoxy pyrazine which can be present in drinking water where it is perceived to be offensive.

Utilities should be concerned about the taste and odour in drinking water because their customers may utilize other sources of potable water that are of questionable quality. For example, Macleans Magazine (1990) published a cover story on drinking water where they reported a 1989 survey showing that 1 in 6 Canadian households use bottled water or a home treatment device. A survey of 37 bottled waters in the United States found that 24 were not in compliance with U.S. drinking water standards (Allen et al. 1991). The authors suggested that it is doubtful that a survey of water utilities would find such a high degree of non-compliance and perhaps consumers are better off drinking tap water. Certainly, the cost of bottled water substantially exceeds the cost of municipal treatment which is currently $0.0011 per litre in Edmonton (City of Edmonton 1993a).

odour episodes because of urban storm runoff, spills, municipal and industrial wastewaters and illicit dumping of wastes.

1.3 Edmonton's Taste and Odour Problems

The North Saskatchewan River (NSR) is the source of water for both of the City of Edmonton's water treatment facilities (Rossdale and EL Smith). Figure 1.1 shows the North Saskatchewan River Basin upstream of the City of Edmonton and Figure 1.2 shows the location of the water treatment plants in the City. The service area for these plants encompasses many small communities surrounding Edmonton for a total service population of approximately 800,000.

Hrudey (1986) found that the water quality of the North Saskatchewan River is generally very good and noted that not many municipalities the size of Edmonton have such a relatively untainted raw water supply. The upstream basin is approximately 27,000 square kilometers and is relatively undeveloped with only three moderately sized municipalities located on the mainstem river between Edmonton and the headwaters at the Saskatchewan Glacier (420 kilometers upstream of Edmonton).

Taste and odour in the City of Edmonton's water supply have been frequently associated with the spring thaw which can occur from late February to late April. During this period, significant amounts of natural organic material are swept into the river by the melting snow. The raw water quality parameters of colour, total organic carbon and turbidity can exceed 100 True Colour Units (TCU), 30 mg/L and 2000 Nephelometric Turbidity Units (NTU) respectively (City of Edmonton 1990).

Sources of this organic material include the biodegradation of plant and animal residues as well as the metabolites of soil micro-organisms. Humic materials, present in the raw water, have very complex structures that include phenol as one of the building blocks. Anderson (1986) found that the total phenolic compounds concentrations in the North Saskatchewan River at Devon maximized at 9 µg/L while levels in Whitemud Creek were 9 to 124 µg/L. These tests were performed using the 4-aminoantipyrine colorimetric method which determines the total phenols as the test responds to most substituted phenols and not the single compound. The total phenols test sums all of the individual phenolic components. As a result, the data should

1.2 Prevalence of Taste and Odour Problems

Virtually every water treatment facility experiences periodic or recurring taste and odour problems in finished water which can generate consumer complaints. A survey conducted by the AWWA indicated that 73% of 120 utilities surveyed experienced taste and odour episodes (AWWA 1976). The origin of these tastes and odours can be natural or synthetic, organic or inorganic, and caused by a single compound or a combination of compounds. To further complicate the identification and removal of the taste and odour, the offending compound(s) can vary from year to year, and season to season.

Taste and odour episodes occur worldwide as shown by Slater and Blok (1983) in their review of cyanobacterially produced odours. Persson (1983) listed taste and odour episodes occurring in Argentina, Australia, Austria, Canada, Czechoslovakia, Denmark, Finland, Germany, Israel, Japan, The Netherlands, Norway, Poland, Sweden, UK, USA and the USSR.

Matsumoto et al. (1988) stated that taste and odour problems have been prevalent in Japan. Taste and odour episodes were experienced by 120 of 300 reservoirs there. They found all of Japan's water supplies from rivers to lakes and ponds to reservoirs were vulnerable to taste and odour outbreaks. Reservoirs which supply water to 13 million people in the greater Los Angeles metropolitan area (McGuire et al. 1983, Means et al. 1986) have had many of the same biologically produced taste and odour compounds. Taste and odour events in the Missouri River have been attributable to the presence of algal blooms and die-offs (Palmer 1980). Wajon et al. (1988) described the problems experienced in an Australian groundwater supply caused by microbially produced sulfur containing compounds.

In Europe, Mohren and Juttner (1983) have described the taste and odour problems of Lake Constance, an important water supply for southwestern Germany. Odour problems in Paris have been so severe, and consumers so demanding, that sensory analysis of the water has been performed every two hours (Montiel 1983). Namkung and Rittman (1987) cited a 1970 survey of British water supplies which found less than one-tenth the potable water supply was free from taste and odour. Paasivirta et al. (1983) described the formation of odorous by-products associated with the chlorine bleaching of pulp in Finland which have found their way to drinking water supplies. Juttner (1988) noted that urban populations can create taste and

Figure 1.1 Upper North Saskatchewan River Basin

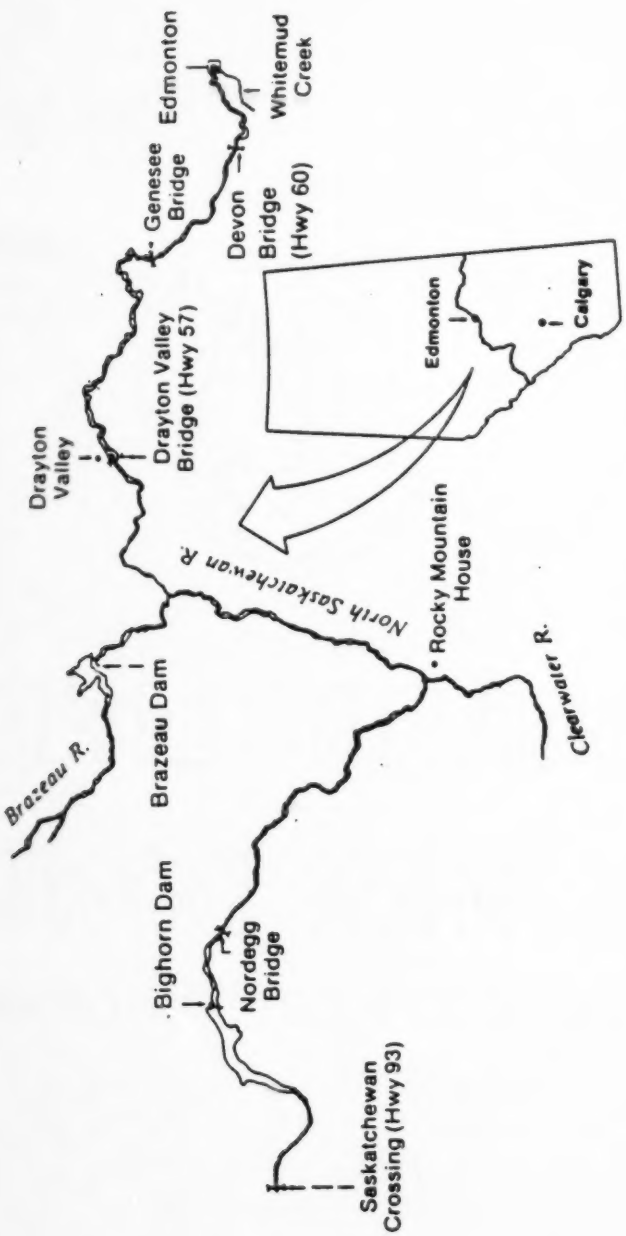
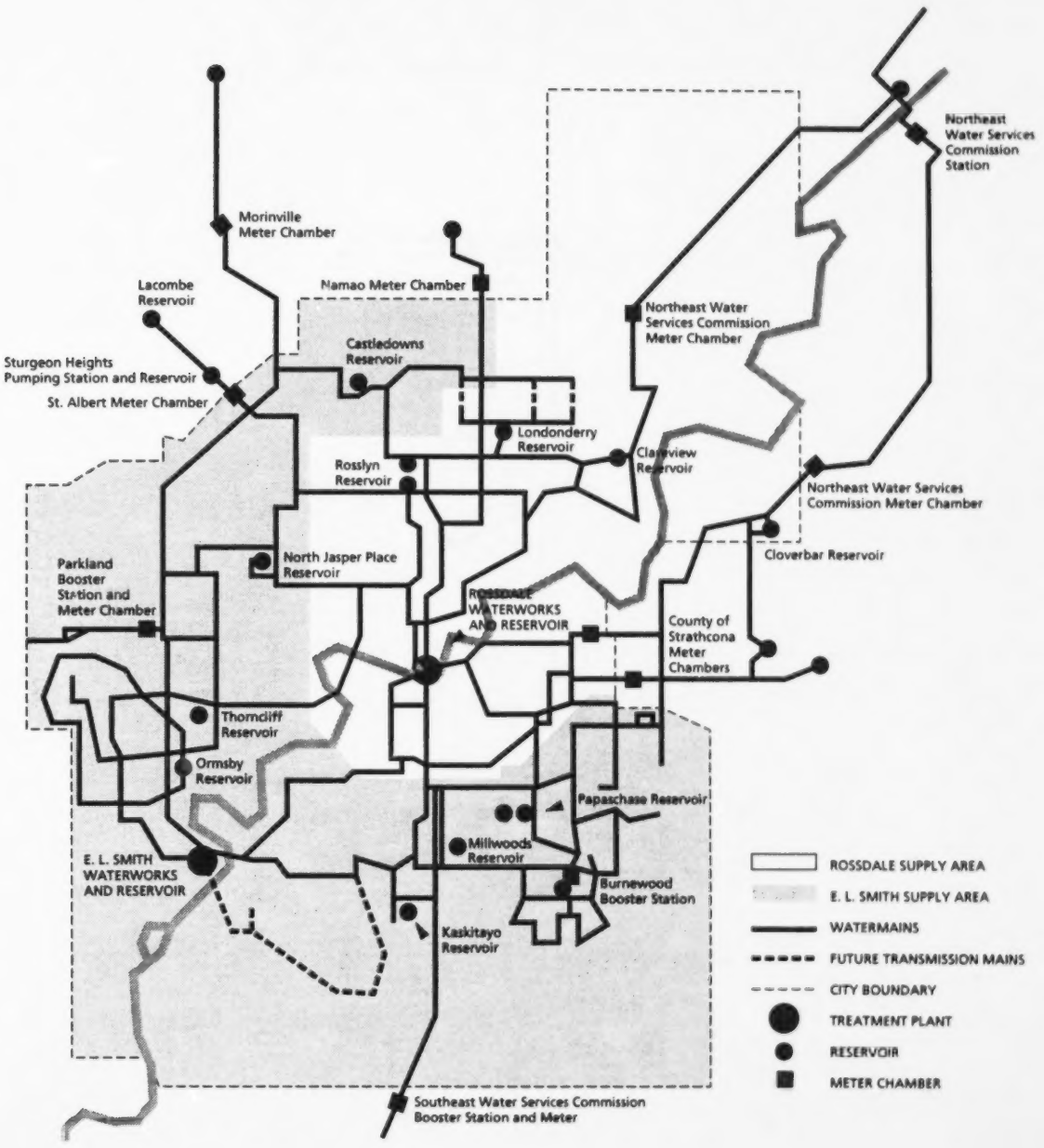


Figure 1.2 Location of the City of Edmonton Water Treatment Plants



be considered minimums as increasing substitution reduces sensitivity (APHA, AWWA, WEF 1992).

During the water treatment process, these phenolic compounds can react with chlorine to form chlorophenols that have much lower odour threshold concentrations than the original phenols. They will generally impart a medicinal odour to the finished water. Walker et al. (1986) have suggested that these compounds could be a source of Edmonton's taste and odour problems. However, data supporting this contention (i.e. chlorophenol concentrations above their OTC's) is limited (Hrudey 1986).

Naturally occurring organics, such as amino acids, readily form odorous aldehydes with many disinfectants (Gac 1988, Hrudey et al. 1988a). Amino acids have been found in Edmonton's raw water supply and odorous aldehydes have been found in the treated water supply in the years 1986 to 1988 (Hrudey 1986, Hrudey et al. 1988a, 1988b, 1989).

During the spring of 1986, the odour data showed that the treated water had a more intense and different odour from the raw water, giving weight to the theory that the odours were being generated in the water treatment plant with the reaction of amino acids and the disinfectants. Stored samples of this water were analyzed and 2-methyl propanal (54 µg/L), 3-methyl butanal (46 µg/L) and 2-methyl butanal (134 µg/L) were found (Envirotest 1986). OTC's for these compounds are 2.3, 2.0 and 12.5 µg/L respectively indicating that they may have been contributors to the taste and odour problem (Amoore et al. 1978).

In the spring of 1988, the Threshold Odour Number (TON) of the raw water was between 2 and 6 whereas the treated water TON was between 20 and 60 (Hrudey 1989). The raw water also had high concentrations of amino acids whereas the treated water contained odorous aldehydes. Although the levels of the odorous aldehydes were frequently below their reported OTC's, they may have contributed to complaints received during the odour event due to the varying sensitivity of the population. As previously noted, when some of these odorous compounds were present at 1/100th their reported OTC's, 4.4% of the population could still detect an odour (Cees et al. 1974). Consequently, aldehydes formed from reactions of amino acids and disinfectants could have been the the causative agents, or contributed to the overall odorous quality of the finished water during this odour event.

Geosmin an earthy, musty smelling metabolite of certain species of cyanobacteria and actinomycetes, has also been suggested as a contributor to taste and odour episodes and was found in single samples of the raw and treated water of both plants at levels of approximately 30 ng/L (Brownlee 1986). The method used, liquid-liquid micro-extraction, has a detection limit of 10 ng/L. As the OTC of this compound has been determined to be less than 10 ng/L (Khiari et al. 1991), this compound could have contributed to the taste and odour problem. Several of the samples Brownlee (1986) analyzed had a camphor like odour. Although mass spectrometer analysis could not confirm the presence of 2-methylisoborneol, a peak at the correct retention times on two different GC columns was obtained. On this basis, 2-methylisoborneol was tentatively identified in several of these samples but the levels were too low to quantify. Because actinomycetes are routinely found in the raw water (City of Edmonton monthly/annual reports 1990) and are ubiquitous in soils and sediments of river margins (Waksman 1959), their role in the production of these earthy/musty metabolites has been suspected.

It has also been suggested that the Brazeau Dam, located 280 km upstream of the City has caused some of the taste and odour problems (Walker et al. 1986). This dam was filled in 1961 without clearing the basin of trees and debris which can be expected to provide soluble organic material as it decomposes. Anecdotal evidence of high colour episodes after large releases from the dam seem to indicate this possibility as the episodes occurred after the approximate travel time from the dam to Edmonton. Burlingame et al. (1986) have also noted that three consecutive releases from an upstream reservoir on the Schuykill River preceded increased concentrations of geosmin. Rizet et al. (1982) have also shown that reservoir discharges have caused taste and odour problems in the Seine and Marne Rivers in France.

The Rossdale water treatment plant is located 17 kilometers downstream of the EL Smith plant in the heart of the City. It is also downstream of 85 storm sewer outfalls, several creeks and 4 bridges. These outfalls pose an additional challenge to plant operators as chemical and microbial contaminants are washed off the roads and into the river with limited dilution. The principle taste and odour problem from this urban runoff has been associated with hydrocarbons from vehicle emissions during the spring thaw as well as during rain events. This can be a significant input

as within the city limits, the outfalls drain approximately 15,000 hectares (Reynoldson et al. 1983).

In the spring of 1978, Van Roodselaar and Walker noted a significant increase in the total volatile organic chemicals during a thaw and speculated it was due to light hydrocarbons trapped in snow formations. In a later study conducted in the spring of 1982, Reynoldson et al. (1983) determined that the cause of Edmonton's taste and odour problem was the loading of the North Saskatchewan River with organics originating from the 85 storm sewer outfalls located upstream. The EL Smith plant was not experiencing any taste and odour problems during this event. They came to this conclusion after measuring 55 chemical parameters (including Dissolved Organic Carbon (DOC) and phenolics) and applying a multivariate analysis to the data (principle component analysis). The analysis showed that phenols were never found at EL Smith but were at Rossdale and on two occasions, concentrations of 6 µg/L exceeded the surface water objective level of 5 µg/L. Storm sewer loadings showed a diurnal pattern with a maximum at approximately 1600 hrs for all compounds tested. Daily loadings of DOC and phenols to the river from all of the upstream storm sewers were determined to be 5150 kg per day and 3.5 kg per day, DOC and phenols respectively, on the 24th of March 1982. The Groat Road outfall accounted for approximately 10% of the total daily loadings for both parameters.

Hrudey (1986) also noted the impact of hydrocarbons on the organoleptic quality of the finished water. Figure 1.3 presents volatile organic compound (VOC) levels from the spring of 1992 at the Rossdale plant which was exposed to urban runoff. Only the Rossdale plant demonstrated high and varying VOC levels while VOC levels at EL Smith were generally non-detectable over the same period. The diurnal pattern resulted from daytime heating and thawing of the snow and ice on the streets and in the sewer system.

During the spring of 1986, Hrudey (1986), found that differences in water quality between the Rossdale plant and the EL Smith plant were even more pronounced when the results of the extractable organic analyses were compared. This analysis provided an assessment of the less volatile components, many of which can impart, or react with treatment chemicals to impart, taste and odour to the finished water. In addition to the two water treatment plants, Figure 1.4 also includes the extractable organic data for the

Figure 1.3 VOC Data from the Rossdale Plant
(City of Edmonton 1992)

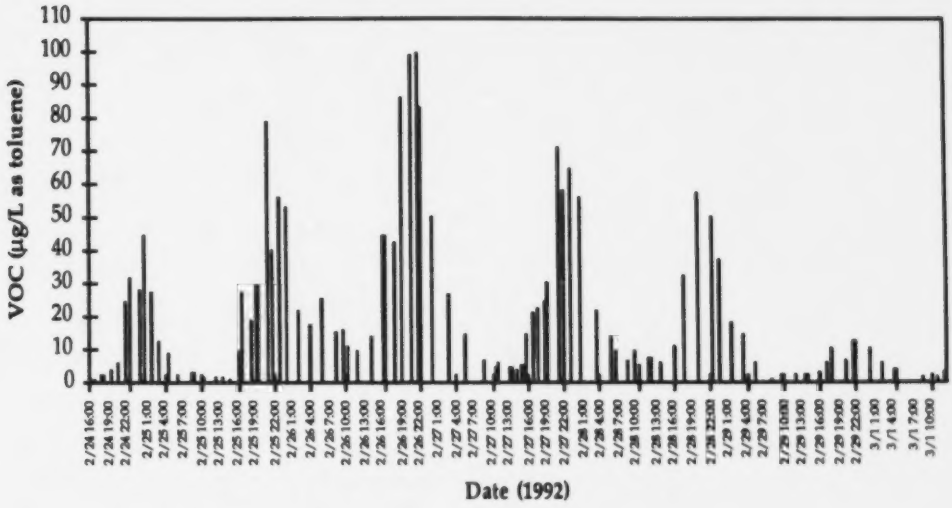
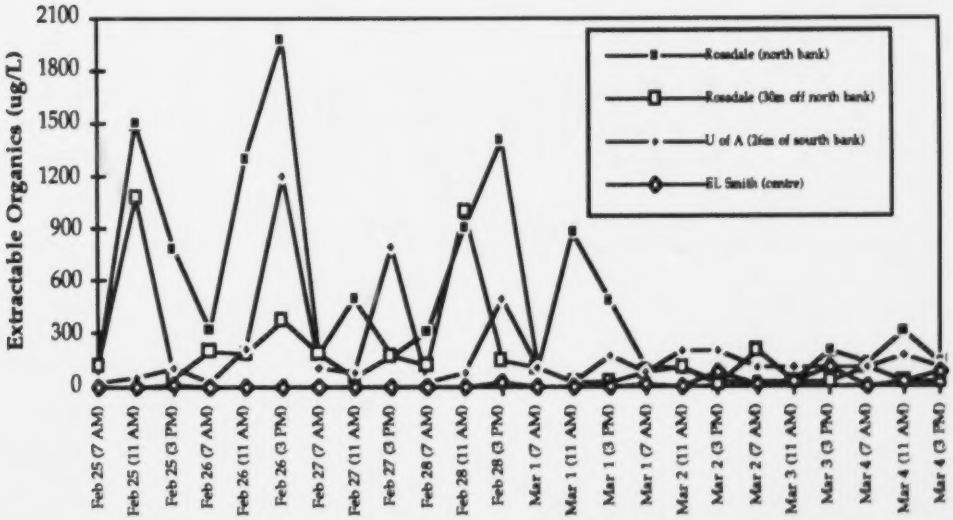


Figure 1.4 Extractable Organic Analyses - February 25 to March 4, 1986
(after Hrudey 1986)



University of Alberta intake located approximately 26 metres off the south bank and 30 minutes upstream of the Rossdale intake.

Much of the organic material detected in the volatile and extractable organic analyses was caused by hydrocarbons arising from gasoline, diesel and oil washing off of the streets. These products possess relatively low odour threshold concentrations which can affect the palatability of the finished water as without powdered activated carbon adsorption, the processes used are inefficient in removing them. Even with PAC, hydrocarbons pass through the process as has been noted by the frequent oil odour detected in routine Flavour Profile Analyses of the Rossdale treated water (Rector 1992). Odour threshold concentrations of oil (0.0005 mg/L) and gasoline (0.01 mg/L) are relatively low and can be expected to cause taste and odour problems during spring runoff and storm events.

At the water treatment plants there are also other sources of taste and odour. Hrudey (1986) noted that plants 1 and 2 at the Rossdale plant were exposed to sunlight and have experienced severe algae growth. These blooms may have caused a number of tastes and odours including fishy as noted by Walker et al. (1986). Chlorine dioxide use on the raw water has eliminated these growths.

Analysis of the taste and odour event of 1986 indicated that the treated water possessed musty, woody, bleachy and swampy descriptors. In March of that year, the chlorine dioxide dosage reached 2.75 mg/L because of a high oxidant demand and the operational procedures which called for the maintenance of a disinfectant residual (i.e. ClO_2) after softening. A maximum dosage of 0.5 mg/L was set by Alberta Environment on March 5 to control the presence of chlorate and chlorite ions in the treated water. Threshold odour number analyses peaked at approximately 130 and the event closely followed the rise of dissolved organic carbon with both plants being equally hit with the same odour.

Trussell (1986) also noted that the nitrogen balance of the plant was not being monitored and that ammonia, and subsequently chlorine, were added without regard to the optimum stoichiometry for the generation of monochloramine. The nitrogen rich environment in the distribution system could conceivably promote the formation of organonitrogen compounds or biological growths whose metabolites could also be a source of taste and odour.

1.4 Statement of the Problem

The ultimate goal of this research was the identification of the taste and odour causing compounds that have caused Edmontonian's to question the safety of their water supply. As discussed in section 1.3, the taste and odour problems in Edmonton's finished water supply may arise from a number of sources and may be due to a number of compounds. In order to fully characterize the odour, a number of techniques have to be employed as the offending compounds have different physical and chemical properties. The first step in this endeavour was the identification of the various techniques that have been successfully employed in other jurisdictions to solve taste and odour problems. These techniques were then used to provide direction for further research efforts.

2.0 Technical Background

2.1 Sources of Taste and Odour

2.1.1 Biogenic Sources

Taste and odour can be produced from a number of micro-organisms including actinomycetes, algae, fungi, moulds, and other bacteria, as well as nematodes and crustaceans. However, the most serious taste and odour problems are generally associated with algae and actinomycetes that produce geosmin and 2-methylisoborneol (Hoehn, 1988). These organisms can be found in water, sediments, attached to plant material and debris as well as inside the cells of other species. In a 1983 AWWA study, 92% of respondents cited decaying organic matter and viable algae as the main causes of odour in raw water supplies (Raman 1985).

A significant problem in determining the organism(s) responsible for taste and odour problems is the interaction between species. The species in the largest numbers at the time of an event may not be the one that produces the taste and odour. An example of this was the initial conclusion that algal blooms were responsible for some taste and odour problems in lakes and reservoirs (Gerber 1979). Subsequent investigations showed that the taste and odour was produced by actinomycetes that were growing in and on the *Cladophora*.

Another problem in taste and odour investigations was noted by Persson (1988a) who found that only 6 of the 42 algal cultures said to produce taste and odour were axenic (pure cultures). The other 36 cultures could have other taste and odour producing organisms such as actinomycetes present which, although in lower numbers, could be responsible for the observed odour. Persson (1988b) further stated that the presence of the bloom coincident with a taste and odour event is not enough to demonstrate there was a cause and effect. There must be a more thorough scientific approach. Juttner (1983) noted there are problems with analyzing axenic cultures as they frequently grow poorly and trace contaminants in the medium can be metabolized by the algae. This atypical nutrition source can alter the production of taste and odour compounds.

2.1.1.1 Actinomycetes

Actinomycetes are filamentous bacteria common to soil habitats. Consequently, they are also found in lakes and streams as they arrive from erosion. Some species of actinomycetes are best known for their production of antibiotics such as streptomycin but they also play a major role in the decomposition of cellulose. As plant debris is ubiquitous around lake and stream margins, they can be expected to be present in aerobic water in large numbers.

Actinomycetes can be isolated from sediments, water in streams and lakes, and can grow on the surfaces or within the cells of living plants. In their study, Niemi et al. (1982) found that river water contained more actinomycetes than lake water as the river water eroded microorganisms from the surrounding stream bed. Waksman, in his 1959 review, cited numerous studies where the numbers of actinomycetes in river bottoms (sediments) are 10 to 1000 times greater than in the water column (up to one million cells per gram of dry material). He also noted that actinomycetes are widely distributed in nature and account for a large part of the normal microbial population in soils, lake and river muds. Silvey and Roach (1975, 1953) however, proposed that many of the taste and odour producing actinomycetes found in drinking water supplies were uniquely different from the soil forms of actinomycetes. Cross (1981) stated that the majority of actinomycetes genera are common and widely distributed in soils especially when the soil is dry, not too acidic and rich in organic matter. They can also proliferate in water (lakes and river margins), in distribution systems (Silvey and Roach 1975) and on most types of biological material (Dougherty et al. 1966). They can survive in the distribution system as they are more resistant to chlorination than most vegetative bacteria (Silvey and Roach 1975). Jensen et al. (1994) isolated actinomycetes from the distribution system of the City of Edmonton. Two of these isolates were able to convert 2,4,6-trichlorophenol, a potent taste and odour causing chemical with an OTC of 100 µg/L (Kovacs et al. 1984), into 2,4,6-trichloroanisole which has a reported OTC significantly lower at 3×10^{-4} µg/L (van Gemert and Nettenbreijer 1977). Cross (1981) noted that the soil actinomycetes can be washed into the water during rain events, with the odoriferous compounds associated with them. Wood et al. (1983b) reported on the ability of streptomycete isolates to produce geosmin when exposed to sterilized debris sediment or soil. Grass and straw surrounding a

reservoir were found to produce 6.70 and 2.44 mg of geosmin per kilogram of dry material. Yagi et al. (1987) found that their streptomycetes isolates were able to produce 156 µg/L of 2-methylisoborneol and 56 µg/L of geosmin.

Actinomycetes have a life cycle composed of an anaerobic phase and an aerobic phase during which odour compounds are produced. Roach and Silvey (1958) found that the taste and odour produced by actinomycetes had descriptors of fishy, grassy and hay-like during the early growth stages and woody, earthy and potato bin in mature cultures. An actinomycetic isolate develops a primary submergent mycelium when inoculated into a broth. This primary stage is microaerophilic (requiring only small amounts of oxygen for growth) and normally lyses in 5 to 7 days. The filaments range from 0.2 to 0.6 µm in diameter. A secondary mycelium then develops, at first as a surface pellicle that changes colour (usually a shade of gray or tan) with age. This secondary mycelium is stable, sporulative, aerobic, and taste and odour compound producing. The filaments and spores range from 0.6 to 1.5 µm in diameter (Silvey and Roach, 1975).

Table A.1 (Appendix A) lists the taste and odour compounds known to be produced by actinomycetes. Hoehn (1988) cited numerous studies where taste and odour production has been linked to actinomycetes and where they have been recovered from water and sediments in lakes and streams. He noted that the taste and odour intensity does not usually correlate well with the actinomycete population in either the water or sediment. This is due to the actinomycetes forming spores. These non-odorous inactive spores can be counted but they will not be proportional to the perceived odour that depends on the production of odorous secondary metabolites by viable organisms.

Collins and Gaines (1964) studied the odours produced by *Streptomyces odorifer* which produced a number of compounds which might make up the earthy odour characteristic of this organism. They noted that this organism may contribute to the foul or pigpen like odours found in water where it was present. They purged a culture grown in an Erlenmeyer flask and used traps which would indicate the functionality of the sulfur containing compounds. As examples, cadmium sulfate traps were used to selectively remove hydrogen sulfide and mercuric cyanide traps isolated dry mercaptans. They found hydrogen sulfide and other sulfur containing compounds but the concentrations were too small to be identified by this method. Collins (1971)

found that actinomycetes could produce cadin-4-ene-1-ol which has a woody earthy aroma.

2-Isopropyl-3-methoxypyrazine, a metabolite of one strain of actinomycete, has an OTC of 2 ng/L and is more volatile than geosmin or 2-methylisoborneol indicating greater potential losses during solvent removal in the sample concentration step. Other compounds that were isolated were furfural (putrid), 1-phenyl-2-propanone, 2-phenylethanol, phenol, mucidone (weak fruity), salicyaldehyde or hydroxybenzaldehyde, and volatile lactones.

Hoehn (1988) found that actinomycetes have caused taste and odour problems when it appeared that an algae problem was under control. The most serious earthy musty odour produced by algae/actinomycete is caused by geosmin and less often, 2-methylisoborneol. Hoehn further stated that occasionally, reservoir shorelines may expose benthic algal mats during droughts causing the algae to die. The decomposing algae may be invaded by actinomycetes which can produce geosmin in high concentrations. Also, since geosmin production by actinomycetes occurs under aerobic conditions, exposed sediments along the shoreline during periods of low rainfall may contain large amounts of geosmin. Later, when the level of the reservoir rises, the geosmin enriched sediments and decaying algal mats will be inundated with water and concentrations of geosmin and 2-methylisoborneol can increase markedly in a short time due to leaching.

Gerber (1979) found that species of actinomycetes produced geosmin, 2-methylisoborneol and 2-isopropyl-3-methoxypyrazine. Others have shown that actinomycetes produced 2-phenyl ethanol, phenol-3-octanone, salicyaldehyde, 2-isopropyl-3-methoxypyrazine, simple amines, short chained aldehydes and saturated fatty acids (Cross 1981, Dougherty et al. 1966). Medsker et al. (1969) isolated three species of actinomycetes and extracted them with steam distillation to obtain 2-methylisoborneol whereas Rosen et al. (1968) found geosmin to be the odorous metabolite of *Streptomyces griseoluteus* IM 3718. Silvey and Roach (1975) noted that actinomycetes produced 5-methyl-3-heptanone as well as geosmin and 2-methylisoborneol. Wood et al. (1983a) noted that *Streptomyces albidoflavus* was prevalent in a reservoir in the UK. This species grew best when in sediment or near plant debris.

Given the widespread occurrence of actinomycetes, and the low OTC's of their metabolites, it is not surprising that early researchers have suspected

that they were responsible for taste and odour episodes. Studies implicating actinomycete produced taste and odour compounds have occurred on the River Nile in 1929, Delaware River in 1934, Salmon Stream in the British Isles in 1936, Moscow River in 1936, River Platt in Argentina and the American southwest in 1938 (Gerber 1979).

In the spring and summer, Dougherty et al. (1966) isolated two genera of actinomycetes (*Micromonospora and Streptomyces*) at a time when utilities were experiencing severe musty taste and odour in the Cedar River in Iowa. The average TON during this period was 896 with a maximum of 4000 (Gerber 1983). After isolation by steam distillation, the odorous chemical was thought to be mucidone based on the deduced chemical formula. It is now thought that the extract was contaminated with geosmin (Mallevialle and Suffet 1987).

Lind and Katzif (1988) noted that the drinking water supply of Waco Texas has had earthy tastes for the past 20 years. These episodes last for 1 to 3 weeks between March and October. They have developed a correlation between rainfall events and taste and odour problems with a lag time of 2 weeks between the rain event and the onset of the taste and odour problem. They suggested that the taste and odour event was caused by either the input of taste and odour producing organisms or environmental agents, which act as nutrients, into the reservoir. Their previous work noted that actinomycetes isolated from the reservoir did not grow without the addition of inorganic nitrogen. They found that the concentration of nitrogen supported an increase in geosmin production. Nitrogen can enter the system from direct rainfall, watershed runoff, wastewaters and nitrogen fixation by cyanobacteria. Their laboratory data supported field observations that taste and odour episodes occurred after rainfall events which supply nitrogen pulses to the reservoir.

Vajdic (1971) stated that actinomycetes would not be a problem for Canadian water utilities as source waters are at temperatures below 4 °C in winter. This conclusion neglected the generation of taste and odour compounds in the fall and the subsequent release during spring melts. Morris (1962) and Erdei (1963) have shown that these types of problems arose in their studies of spring taste and odour problems in Midwestern rivers.

2.1.1.2 Algae

There are numerous types of algae that are found in surface water supplies (lakes, reservoirs, rivers and streams). Many of these have been implicated as the cause of taste and odour problems in potable water. These organisms include cyanobacteria (blue-green algae), green algae, diatoms and flagellated algae. They can exist as plankton or attached to sediments as benthic mats. They can also form bio-films on rocks and higher plants.

Palmer (1980) noted that practically all of the taste and odour episodes in the Missouri River coincided with the presence of algal blooms and the few exceptions came during the declines of dense algal growths. Hattori (1988) and Hishida et al. (1988) describe the problems of 19 water treatment plants serving 19 million people in Japan. These plants, located on the Yodo River and Lake Biwa, have been colonized by cyanobacteria causing taste and odour problems since 1969. Tsuchiya and Matsumoto (1988) noted that 40% of Japan's water sources (rivers, lakes, ponds and reservoirs) have an unpleasant earthy musty off-flavour. Berglind et al. (1983a) found that algae caused most Norwegian taste and odour problems and that actinomycetes only played a secondary role.

Table A.2 lists the identified odorous compounds attributed to algae with odour descriptors and odour threshold concentrations.

Slater and Blok (1983a), in their review of cyanobacteria and volatile metabolites, found that the first indication of a correlation between taste and odour episodes and algae was reported in 1883. Their review documented that various cultures of cyanobacteria can produce a wide range of chemical substances, many of which can impart an off-flavour to potable water supplies. These compounds included geosmin, 2-methylisoborneol, aliphatic hydrocarbons, esters, fatty acids, amines, aromatics, terpenoid compounds and sulfur containing compounds. The cyanobacteria *Microcystis*, has been known for its ability to produce large quantities of ß-cyclocitral (Juttner 1988). Matsumoto et al. (1988) found *Oscillatoria amoena* in a river water supply in Tokyo. Hayes and Burch (1989) determined the taste and odour problems of several reservoirs and the River Murray were due to the metabolites of *Oscillatoria, Anabaena flos aquae, Microcystis aeruginosa* and the chrysophyte, *Synura petersenii*. They provided an extensive list of the compounds they were able to identify from each of the species. Henatsch and Juttner (1983) extracted six species of *Synechococcus* to obtain alcohols,

ketones and terpenoid derivatives. In Germany, Mohren and Juttner (1983) isolated alcohols, aldehydes and alkenes from *Anabaena* and *Nostoc* cyanobacteria. Juttner (1983, 1988) reviewed the by-products of biogenic activity in surface waters. He listed numerous compounds within the following structural groups: alkenes, olefins, nor-carotenoids, isoprenoids, aldehydes, sulfur containing compounds, esters, saturated and unsaturated aliphatic alcohols, ketones, thioesters and sulfides.

Berglind et al. (1983a, 1983b) found *Oscillatoria* spp. in lake and river systems that produced large quantities of geosmin. They also showed that the decaying algae produced an especially obnoxious taste and odour problem caused by the breakdown of proteins. Burlingame et al. (1986) presented their interesting experiences with the Schuylkill River in Philadelphia. During a drought, causing low water flow, the geosmin level reached 100 ng/L leading to many consumer complaints. The algae was able to colonize the river and the cells trapped air bubbles, floated to the surface and collected in the bend of the river where the intake was located.

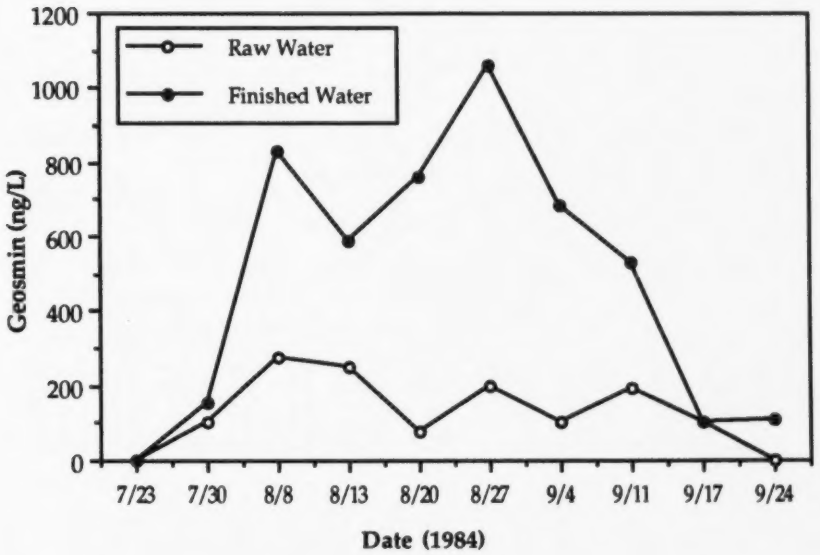
Gammie et al. (1988) noted that during a cyanobacterial bloom, the levels of geosmin were higher in the finished water than in the raw water (Figure 2.1). This was due to the prechlorination required to prevent algae growth in the pipe from the source to the plant. Chlorination lysed the algal cells releasing the metabolite geosmin. Others (Ashitani et al. 1988) have also found that pre-chlorination increases the concentration of odorous metabolites (geosmin and MIB). At Buffalo Pound in Saskatchewan, Canada, Brownlee et al. (1988) showed that even after granular activated carbon treatment, the levels of geosmin remained high.

Reservoirs in California have demonstrated large increases in the 2-methylisoborneol concentration which Izaguirre et al. (1982, 1983) attributed to the cyanobacteria *Oscillatoria curviceps*.

A bio-mass of *Cladophora* studied by Brownlee et al. (1984) showed that sulfur containing compounds such as indole, 3-methyl indole (skatole) and dimethyl polysulfides were present and they speculated that these may be caused by the anaerobic decomposition of the algae. Slater and Blok (1983a) have also shown sulfur containing compounds, such as 3-methyl indole, to be present in river systems contaminated with *Oscillatoria* spp. Jenkins et al. (1967) analyzed cyanobacteria cultures containing *Microcystis flos aqua*, *Oscillatoria chalybia* and *Anabaena* spp. and found the presence of sulfur

containing compounds such as mercaptans and dimethyl polysulfides. Dimethyl trisulfide has been shown to be the cause of the fishy, swampy odours in California. Krasner et al. (1989a) found that the recycling of filter backwash water concentrated the diatom *Stephanodiscus* which produced dimethyl trisulfide.

Figure 2.1 Geosmin Concentrations at Buffalo Pound WTP
(after Gammie et al. 1988)



2.1.1.3 Other Organisms

Although the majority of microbial induced taste and odour episodes have been caused by algae and actinomycetes, other organisms are capable of producing an off-flavour (Hoehn 1988). Table A.3 lists various metabolites of organisms known to cause taste and odour problems.

Niemi et al. (1982) have shown that fungi proliferate in eutrophic water systems, especially rivers. Fungi have been shown to produce odorous

metabolites such as geosmin and 2-phenylethanol (Kikuchi et al. 1981, Mallevialle and Suffet 1987, Maga et al. 1987).

Krasner (1988) noted that certain microbes can methylate chlorophenols produced in the chlorobleaching of pulp to produce chloroanisoles whose odour threshold concentrations are 2 to 9 orders of magnitude lower than their precursors. Nystrom et al. (1992) have shown that fungi and actinomycetes isolated from distribution systems in Sweden could methylate 2, 4, 6-trichlorophenol formed during the disinfection (chlorination) process, to produce 2, 4, 6-trichloroanisole. They demonstrated that this trichloroanisole made a significant contribution to the overall odour character of the finished water.

Wajon et al. (1988) isolated 108 species of bacteria including *Pseudomonas* and *Flavorbacterium*, in an Australian groundwater supply. Bacteria were also found in the distribution system and in much higher concentrations in the pipe wall sediments. These organisms were responsible for the production of dimethyl polysulfides which caused an unpleasant, cooked vegetable type odour. The investigation also indicated the presence of algae, actinomycetes, fungi and yeasts.

Pseudomonas has been shown to produce septic sewer-like odours caused by the conversion of natural amino acids to mercaptans and dimethyl polysulfides (Whitfield and Freeman 1983).

Crustaceans (microscopic invertebrates), such as *Daphnia* and *Cyclops*, and the rotifer, *Keratella*, have all been linked to fishy odours in water when their population densities are high (Lin 1977).

2.1.2 Abiotic Sources

Abiotic sources of taste and odour causing compounds include urban runoff, municipal and industrial wastewaters and rural runoff associated with herbicide and pesticide use. Virtually any chemical in use (or in some cases, historically used) can cause a taste and odour problem caused by improper use, storage or spill. Although many of these compounds have higher odour threshold concentrations than geosmin or 2-methylisoborneol, they may be responsible for taste and odour episodes as they are used or produced in significantly higher concentrations. Table A.4 lists several abiotic sources of taste and odour.

In Ontario, Williams (1976) stated that the Grand River was an odorous river and that it received raw sewage, partially treated sewage, activated sludge plant effluents and a host of industrial effluents. Becker (1976) noted that the most consistent odour in Indianapolis river supply was that from municipal discharges upstream. Municipal wastewaters can contain phenols, fatty acids, aromatics, chlorinated solvents such as tetrachloroethylene and polychloroanisoles which can impart taste and odour to the drinking water supply as the odour threshold concentrations are so low (Mallevialle and Suffet 1987).

Chlorophenolics are produced in the bleaching of pulp with chlorine (Krasner 1988). These compounds have odour threshold concentrations in the low µg/L range for the dichloro species and may therefore impart taste or odour to water (Faust and Aly 1983). Paasivirta et al. (1983) stated that chlorobleaching of pulp is the largest source of persistent pollution in the aquatic environment because of the stability of the organohalogen compounds. They noted that in Finland 80,000 tons/year of organohalogens are released that originate from lignin, terpenes and fatty acids. The compounds that are produced include chlorophenols, chloroguaicols, chlorocatechols and chloroanisoles. Some of these compounds, such as 2,3,6-trichloranisole, have odour threshold concentrations reported to be as low as 0.001 ng/L (Paasivirta et al. 1983, Van Gemert et al. 1977). However, the more generally accepted odour threshold concentrations are in the range of 0.1 ng/L with the differences caused by varying sensitivity of panels and sample purity.

Gasoline and petroleum products from urban runoff or spills can have a dramatic effect on the quality of the finished water. These mixtures contain benzene, xylenes, toluene and other substituted benzenes (Juttner 1988). The rapidly expanding urban infrastructure upstream of the water works in Atlanta caused frequent taste and odour events due to spills of oil and related products (Peters 1976).

Montiel (1983) noted an increase in taste (oil and petroleum) of the potable water supply which coincided with the opening of a new power station upstream which was releasing wastes. Mallevialle and Suffet (1987) listed odour threshold concentrations for selected crude oils and petroleum products. They ranged from 0.5 µg/L for Nigerian light crude and diesel fuel to 10 µg/L for gasoline and Kuwaiti crude.

Suffet et al. (1980) analyzed water extracts from the City of Philadelphia and found that most of the compounds were likely of an industrial origin. Compounds such as tetrachloroethylene, esters, substituted benzene isomers and naphthalene were found.

2.1.3 Water Treatment Generated Odours

Current water treatment practices, principally disinfection, can cause taste and odour problems. Stevens et al. (1989) chlorinated natural and humic acid spiked water and detected more than 500 disinfection-by-products. Chlorination of phenolics leads to the formation of compounds with significantly lower odour threshold concentrations (Bartels et al. 1986a, Krasner et al. 1985, Namkung et al. 1987). Residual chlorine, chlorine dioxide and chloramines are also objectionable to some.

Hrudey et al. (1988a, 1989) have shown that low levels of aldehydes with odour threshold concentrations in the low µg/L range, producing swampy odours, were formed through the oxidation of naturally occurring amino acids. Amino acids that were found to produce the corresponding aldehydes were valine, leucine, isoleucine and phenylalanine. Bruchet et al. (1992) confirmed these results and also found that alanine, methionine and peptides produced objectionable odours following chlorination. These investigators have noted that the amino acids and peptides are by-products of natural processes and represent a high taste and odour potential where chlorination is practiced. Table A.5 lists treatment stream generated taste and odour compounds.

de Greef et al. (1983) found that odorous compounds were formed from the bituminous materials used as protective coatings. The City of Edmonton noted that large quantities of volatile compounds were leached from coatings (coal tar epoxy) in new pipelines lasting for longer than six months. Manufacturers claims of improper curing were shown to be incorrect (City of Edmonton 1977). Anselme et al. (1985a, 1985b) showed that polyethylene pipe leached a variety of chemicals that imparted a plastic or burnt plastic taste and odour. Hansson et al. (1987) showed that the order of chemical addition to form chloramines is important in the reduction of taste and odour. They originally applied ammonia prior to chlorine addition but they found that the production of iodoform (medicinal/plastic taste) to be at 8 µg/L. After

reversing the order, they reduced the iodoform concentration to below 1 µg/L which is below its OTC of 5 µg/L.

Advanced water treatment processes have been shown to produce odours in the finished waters. Anselme et al. (1988) found that ozone produced high intensity fruity odours caused by the production of aliphatic aldehydes and benzaldehyde. They demonstrated that the intensity of the fruity odour was proportional to the log of arithmetic sum of the aldehydes (C_6 to C_{11}) present. Glaze et al. (1989, 1990) showed that there were negative removals of hexanal and heptanal when using chlorine dioxide, chloramines, hydrogen peroxide - UV and ozone. Their ozone studies indicated that ozone produced up to 2 µg/L of these compounds, above the OTC of hexanal which is 0.5 µg/L (Van Gemert et al. 1977). Other aldehydes were also produced.

In a study for the AWWA RF, Dietrich and Hoehn (1991) found that chlorine dioxide was reforming in the distribution system and causing tastes and odours. The mechanism for this reaction could not be determined. They also found that the residual chlorine dioxide was volatilized at the tap and reacting with chemicals (such as those from new carpet) in the homes of consumers to produce cat urine and kerosene-like odours. The odorous compounds responsible for these odours were not identified.

Nystrom et al. (1992) studied groundwater and river sources in their taste and odour investigations. They found that both raw water sources generated low levels of 2,4,6-trichlorophenol such that they were below the odour threshold concentration of 0.1 mg/L (Kovacs et al. 1984). However, actinomycetes and fungi present in the distribution system were able to methylate this compound and convert it to the much more odorous 2,4,6-trichloroanisole (OTC 0.03 ng/L). They also stated that 2,4,6-trichlorophenol can be produced even when chlorine dioxide and chloramines are the disinfectants. Jensen et al. (1994) have found that the actinomycetes present in the finished drinking water could also methylate trichlorophenol in the City of Edmonton's distribution system.

2.2 Analytical Methods

2.2.1 Concentration Methods

The extremely low levels of some contaminants in drinking water associated with taste and odour episodes has usually necessitated their concentration prior to analysis. Geosmin, with an odour threshold concentration in the low ng/L range, is one such compound that has been qualitatively and quantitatively identified utilizing various concentration methods such as sorbent adsorption, stripping analysis, liquid-liquid extractions and preparative gas chromatography. In using these techniques, the detection limits of some of these taste and odour causing compounds have been reduced to nanogram/L levels allowing utilities to monitor the onset of an off-flavour episode as well as to determine the effects of various process changes on contaminant levels. The changes in water quality associated with treatment modifications can be determined at such low levels that remedial action can be taken prior to the event being noticed by the consumer.

Each of these concentration methods listed here have their strengths and weaknesses. Their application at a specific site is dependent upon the following factors:

1. requirement for specific or broad spectrum analysis
2. volatility of odorous compound
3. solubility of odorous compound
4. concentration of odorous compound
5. partition coefficients (air-water, solvent-water, sorbent-water)
6. availability of equipment and trained personnel

Most problems arising with taste and odour require the use of the broad spectrum approach especially when the season to season, or year to year characteristics of the problem vary. In certain circumstances, where the source of the problem is well known, specific methods for target compounds may be employed. Budde and Eichelberger (1979) noted that methods for the analysis of organics should be considered complementary rather than strictly competitive. One method is unlikely to be the panacea for all taste and odour analysis problems. Several methods should be employed simultaneously if the nature of the odour problem in not well understood.

2.2.1.1 Sorbents

Sorbents have been used extensively to concentrate organics found in raw and treated water. There are two general classes, activated carbons and synthetic resins. The use of resins is a three step process, the adsorption of the organics from the water, desorption of the solute from the sorbent and the reduction of the resulting extract for further analysis. This final step will be covered in section 2.2.1.3. Table 2.1 contains various physical characteristics of several widely used carbons and resins. Note that XAD refers to a series of resins produced by Rohm and Haas.

Table 2.1 Physical Characteristics of Commonly Used Sorbents

Sorbent	Chemical Structure	Surface Area (m^2/gram)	Average Pore Diameter (Å)	Dipole Moment
Synthetic Polymers				
XAD-1	Styrene DVB	100	200	
XAD-2	Styrene DVB	300	100	0.3
XAD-4	Styrene DVB	725	48	0.3
XAD-7	Acrylic ester	450	85	1.8
XAD-8	Acrylic ester	160	150	1.8
XAD-9	Sulfoxide	69	366	3.9
XAD-11	Amide	69	352	3.3
XAD-12	Nitrogen Oxy	22	1300	4.5
XE-284	Sulfonic Acid	571	44	>5.0
Activated Carbons				
Nuchar WV-L	Coal	1000		
F-300	Coal	950-1050		
Hydrodarco	Coal	600-650		

XAD data from Amberlite Resin Selection Guide Supelco Canada Oakville Ontario 1990
Activated carbon data from Van Waters and Rogers 1979

One of the major problems associated with using a sorbent to concentrate organics from water is the adsorption/desorption procedure. Ideally, the sorbent would quantitatively remove the trace chemical from the water and then quantitatively release it during solvent desorption. In practice however, strongly adsorbing sorbents tend to give high percentage removals but low recoveries because much of the trace solute is retained on the sorbent. Conversely, weakly adsorbing sorbents release the sorbed material readily although they only adsorb a small fraction of the chemicals present in the water. Aaberg et al. (1985) have found that different adsorbents with differing

adsorption characteristics often had to be used to obtain a more complete collection of trace substances. Chriswell et al. (1977) used carbon and resin in series (and vice versa) in order to obtain a broader spectrum of organics from the water. Thakker et al. (1987) noted that some compounds are not recoverable by solvent extraction, especially at low loading, as source compounds were irreversibly bound to the sorbent (carbon). In some cases, they found displacers at high concentrations useful to overwhelm the active sites and release the solute.

Jackson et al. (1987) showed that activated carbon can promote the formation of additional by-products not formed by the reaction of disinfectants or organics in aqueous solution as indicated below.

Cl_2 + phenol---------->poly chlorophenols
Cl_2 + activated carbon + phenol---------->chlorohydroxybiphenyls
ClO_2 + ethylbenzene---------->benzylic ketones/alcohols no Cl substitution
ClO_2 + activated carbon + ethylbenzene------->mono and di chloro derivatives

They suggested the mechanism for chlorine dioxide reactivity was the formation of highly reactive chlorine containing species on the carbon surface such as ClO, Cl_2O_3, Cl and HOCl which in turn reacted with the organic material in the water.

Ahnoff et al. (1974) noted that particulates associated with natural waters posed another problem with using sorbents to concentrate organics. Some contaminants became adsorbed to particulates and either passed through the column or restricted the flow. A pre-filter could have been used to remove these particles but the composition of the water would then have changed.

Synthetic resins have been widely used in the concentration of organics from natural and treated waters. A variety of resins have been found to be effective in the concentration of very low levels of contaminants. Lebel et al. (1988) extracted 1500 L of lake water with XAD-2 and recovered pollutants at the 0.1 to 40 ng/L level. Wigilius (1987) also found XAD-2 resin effective for a 32 component cocktail of chemicals with various fuctionalities. These compounds were tested in the 20 to 200 ng/L concentration range. Junk et al. (1974) found the useful analytical detection range of the resin to be from 5 ng/L to 50 mg/L for a range of chemicals when using XAD-2 and XAD-4.

Matsumoto et al. (1988) used XAD-2 to identify the taste and odour producing compounds geosmin and 2-methylisoborneol in 10 L of water. Huck et al. (1987) and Loper et al. (1988) used XAD resins to concentrate organics for mutagenicity studies as well as gas chromatography mass spectral analysis.

Two major studies were found that analyzed and optimized the adsorption, desorption and reduction steps associated with XAD resins (Junk et al. 1974, Wigilius 1987). Both groups noted the importance of ensuring that the resin is scrupulously cleaned prior to use. Wigilius (1987) found that by adding an extra washing step with diethyl ether, they avoided having methanol and water on the resin at the same time. This reduced the blank problems (i.e. artifact generation) by a factor of 30. Junk et al. (1974) found some of the artifacts to be naphthalene, ethyl benzene and benzoic acid which arise from the manufacture of the resin. Blok et al. (1983) suggested that the artifacts may have been generated by the beads fracturing caused by the expansion during water/solvent changes as they were present even after extensive cleanup. Henatsch and Juttner (1983) utilized two types of resins, Tenax and XAD, in order to differentiate between artifacts. Due to the large number of artifacts Blok et al. (1983) found that adsorbents (resins and carbon) were unsuitable as they interfered with GC analysis of the low boiling compounds. In contrast to this, by adding the extra washing step, Wigilius et al. (1985) have found that resins can be used to effectively recover organics from water at the 20 to 200 ng/L levels.

Many researchers cited the positive aspect of using resins as they can be reused after recovery of the organics. However, in their review, Daignault et al. (1988b) noted that there is a problem with the humic material as some 20% of it remains irreversibly bound to the resin.

Junk et al. (1974) used 110 test compounds representing a cross section of chemical properties including alcohols, aldehydes, acid aromatic halides, alkyl benzenes, phenols chlorinated phenols, esters, ethers, ketones, PAHs, herbicides, pesticides and halogen, nitrogen and sulfur compounds. They were tested individually and as a mixture of components and the average recovery was found to be 78% (sd 6.3%). Most of the compounds were well recovered (high 80% or low 90%) with a only a few poorly recovered ones (50 to 60%). They also found the concentration range to be from 5 ng/L to 50 mg/L with very good results at the 10 to 100 µg/L level. They did however, observe a problem with dissociated organics because they are not well

adsorbed because the XAD is non-ionic. All but the largest organic molecules prefer the aqueous phase when they are in the ionic form. Glaze et al. (1989) noted this problem in their work with ozone which tends to produce polar material which will not adsorb well at neutral pH's. In their study comparing resin adsorption, Blok et al. (1983) found that the resins recovered solutes in the following order:

XAD-4 > XAD-2 > Tenax-GC > XAD-8 > XE-340 > XE-348

In order to improve these results, many researchers acidified the water prior to adsorption (Junk et al. 1974, Wigilius 1985, Thurman 1981, Suffet et al. 1980). Noordsij et al. (1983) took the pH adjustment one step further by having 3 cartridges in series with pH adjustment between them. This allowed for the fractionation and adsorption of the neutral, acidic and basic groups.

Granular Activated Carbon (GAC) has not been as widely used as XAD resins because of the high background levels, inconsistent quality, difficulties in desorption and alteration of some compounds (Blok et al. 1983). Rosen et al. (1968) have used carbon filters to recover geosmin and 2-methylisoborneol for mass spectral analysis in their extraction of 3000 L of water.

There are problems associated with using GAC to concentrate organics from water. The background problems with GAC can be severe enough to significantly reduce detection limits (as measured by the signal to noise ratio). Grob et al. (1975) noted that a gas chromatograph has a 0.1 ng/L detection limit in a clean sample, 2 ng/L in a slightly contaminated sample and 100 ng/L in contaminated samples.

Lalezary-Craig et al. (1988) noted that GAC adsorption decreases markedly for geosmin and 2-methylisoborneol in the presence of background humic material or in the presence of chlorine/monochloramine. Lee et al. (1981) has also found that GAC adsorbs humic material very well. Jackson et al. (1987) have shown that GAC can promote the formation of additional products not found in blanks in the presence of disinfectants. This may have been due to the large and varied functional groups on the surface of the activated carbon. Some of these groups include carbonyls, phenolic OH, quinone carbonyls, ethers peroxides, anhydrides and sulfur as noted by Voudrias et al. (1985).

Recovering the sorbed material from the carbon may be difficult as it may be tightly bound to the carbon and in fact may be chemically bound to the surface. Buelow et al. (1973a,b) Soxhlet extracted carbon with two solvents, chloroform followed by ethanol, to try and remove some of the more polar compounds. Chriswell et al. (1977) investigated the use of GAC (and XAD-2) to adsorb organics and found that solvent elution gave similar results as Soxhlet extraction. They also utilized several solvent scenarios and combinations to remove the organics. These investigators found that all of the combinations used were good for some compounds and bad for others, indicating there is no universal solvent for desorption. They also concluded that the resin was superior to the carbon which they found to be less efficient in desorbing the organics in the water.

2.2.1.2 Stripping Techniques

Traditional methods for concentrating and analyzing contaminants possess significant flaws that have limited their usefulness in trace organic analysis, especially for volatile compounds. Stripping techniques were developed to overcome the high backgrounds, artifact generation, excessive sample handling and high volatile losses associated with these methods. The stripping methods have high concentration factors (50,000 times) with small sample sizes of 1 to 4 litres.

There are two main stripping techniques, both of which are now accepted as standard methods (APHA, AWWA, WEF, 1992). The first, closed loop stripping analysis (CLSA), has been shown to be sensitive, reproducible and effective in the analysis of ultratrace levels of odorous organics in the water treatment industry. The second, purge and trap, is essentially an open loop stripping technique that does not recycle the gas flow. Both methods trap the stripped compounds on a small amount of sorbent (carbon, Tenax-GC, ORBO-22). The adsorbed material can then either be extracted with small amounts of solvent (Krasner et al. 1983) or thermally desorbed directly onto a GC or GC-mass spectrometer (Hrudey et al. 1988).

Grob et al. (1975) developed the original design of the CLSA method and Krasner et al. (1983) and others have tried to optimize its use. This method has been used to determine a large number of compounds including:

- esters, lactones, alcohols and aldehydes in fruit (Brunke et al. 1989),
- ozone disinfection-by-products such as aldehydes (Glaze et al. 1989, 1990),
- algal bloom metabolites including alcohols, sulfides and aldehydes (Hayes and Burch, 1989),
- extraction of geosmin and 2-methylisoborneol from algal cultures (Izaguirre et al. 1982),
- other odorous compounds from algal cultures (Mohren and Juttner, 1983),
- 2-methylisoborneol from sediments and rock scrapings (Izaguirre et al., 1983, Krasner et al. 1983),
- fuel spill finger printing (Westendorf 1982),
- analysis of odorous compound reduction with PAC and alternative disinfectants (Lalezary-Craig et al. 1988, Lalezary et al. 1986a, 1986b),
- early warning system as the detection limits are lower than the odor threshold concentrations (McGuire et al. 1983), and the
- determination of dimethyl polysulfides in drinking water (Wajon et al. 1988, Krasner et al. 1983).

Hwang et al. (1984) found that the detection limits of the method could be substantially reduced, down to low ng/L levels for 2-methylisoborneol and other odorous compounds, with the addition of salt. The salt had two effects on the stripping. First, it increased the ionic strength of the solution thereby reducing the solubility of any organic material. Secondly, Hwang et al. (1984) noted that the size of the bubbles from the stripper were smaller with the salt added. This increased the surface area available for gas transfer and reduced the required stripping time. However, Hrudey (1992) noted that the salt has the effect of reducing the adsorption capacity of the carbon cartridges after only four runs.

The purge and trap technique has been used for a wide variety of compounds for a number of years. It has been used for the analysis of a wide variety of chemicals including haloforms (Huck et al. 1988) and other chlorinated organics (APHA, AWWA, WEF, 1992). Yagi (1983) developed a method, open loop stripping apparatus (OLSA), whereby an external pump was used to strip larger samples of 100 mL to 1 litre. He found that he could determine ng/L levels of geosmin in 30 minutes when using thermal

desorption GC-MS of the Tenax. Others such as Hishada et al. (1988), Ashitani et al. (1988) and Miwa et al. (1988) have all successfully used this method to determine geosmin and 2-methylisoborneol in water and algal cultures. Ashitani et al. (1988) used the salt to improve extraction efficiency as well as to lyse the cells of the cultures to release the intracellular material.

Other researchers, Charles et al. (1987), Daignault et al. (1988a), Savenhed et al. (1983), Bellar et al. (1974) and Wigilius et al. (1987) have replaced the pump with compressed nitrogen. Savenhed and co-workers (1983) have noted that the pump can be a source of artifacts and poor recoveries due to leaks at joints. The compressed gas blanks were much cleaner than the pump blanks. Lundgren et al. (1988a) has used this method to determine the taste and odour causing disinfection-by-products of ozonation.

An interesting early example of the use of OLSA with compressed nitrogen is the work by Collins and Gaines (1964). They were attempting to determine what sulfur compounds were causing the odour from certain actinomycete cultures. They bubbled nitrogen through the culture and passed the gas through traps of lead acetate, mercuric cyanide and mercuric chloride to determine the presence of hydrogen sulfide, mercaptans or sulfides/polysulfides respectively. These traps were specific for the associated sulfur containing compounds.

Several researchers have noted flaws in these methods. Lalezary-Craig (1988) has noted that although the detection limits may be low (sub nanogram/L), the precision and accuracy are poor, often greater than ± 20%. In stripping sediments Charles et al. (1987) noted the recoveries of chloroform, trichloroethylene and chlorobenzene ranged from 38% to 54% with losses in water up to 23%. Daignault et al. (1988a) have noted that the method does not have the sensitivity of the PFBOA method (Sclimentti, 1990) for aldehydes although it was relatively convenient and gave reproducible results. Krasner et al. (1989) have noted that the analysis requires approximately 2 hours to complete, not including cleanup or the subsequent analysis. Hargesheimer (1990) and Grob and Zurcher (1976) have noted that the system is prone to losses due to the number of joints and fittings. Hu and Weiner (1980) have noted that there are foaming problems and calibration problems for some components.

Another stripping method that is not widely used in the water treatment industry is steam distillation extraction (SDE) that was developed by Nickerson and Likens (1966). Dougherty et al. (1966) have used this method to extract geosmin from water while Gavinelli et al. (1986) have used it to concentrate volatile nitrosamines. They noted that the sample matrix is processed for analysis in a single step. Tsuchiya and Matsumoto (1988) used this method to concentrate the metabolites of eight cyanobacteria found in rivers, lakes and reservoirs. The water and solvent are boiled in separate flasks and the resulting gases are mixed and cooled with the organic material extracted from the steam into the solvent. The SDE method has been shown to have a wider range of compounds that can be extracted. Juttner (1983) found that CLSA could not isolate thiophenes or polysulfides from sediments whereas SDE could. He also noted that stripping, with SDE, was gentle and likely did not produce the metabolites from within cells. Richard and Junk (1984) have found that the SDE method obtained excellent recoveries for fatty acids, many of which have disagreeable odours at low concentrations.

2.2.1.3 Liquid-Liquid Extractions

Liquid-liquid extractions (LLE) have been widely used in the analysis of organic contaminants in water. A wide variety of compounds can be determined as noted in Standard Methods for the Examination of Water and Wastewater, 18th Edition (APHA, AWWA, WEF, 1992).

The method is based on the principle that when exposed to an organic solvent, each organic compound in water would partition between the two solvent phases depending upon its relative solubility in each phase. The difference in the dipole moments of the solute and solvent can be used as an index to the extraction efficiency (Goldberg and DeLong 1973). Suffet and Faust (1972) developed a method to express the distribution of solutes in order to compare efficiencies of various water to solvent ratios.

Suffet et al. (1980) identified over 100 compounds in river water by LLE. The method has achieved widespread use and acceptance in the analysis of taste and odour as it can extract volatiles such as the haloforms (Richard and Junk 1977) as well as semi-volatiles such as phenols and polychlorinated biphenyls. Yamada and Somiya (1989) and others have used a liquid-liquid extraction for the analysis of odorous short chain aldehydes using the pentafluorobenzylhydroxylamine (PFBOA) method. The appeal of this

method has been that the samples are derivatized and can be analyzed directly by GC-electron capture detection which is more sensitive for electronegative compounds than either flame ionization detection or mass spectrometry. Matsumoto et al. (1988) extracted geosmin and 2-methylisoborneol (0.03 µg/L to 3.6 µg/L) from 10 litres of river and lake water with ether. Slater and Blok (1983) extracted these odorous compounds in water caused by cyanobacterial blooms. Brownlee et al. (1984) used LLE to isolate geosmin and sulfur compounds such as 3-methylindole, sulfur and dimethyl polysulfides. Brunke et al. (1989) found that solvent extraction recovered a larger number of compounds and odours (as measured by GC-sniffing) than CLSA. This work with natural products found in fruits has the same problems as water research has with determining the causes of odour (i.e. the odour problem has more than one compound combining to cause an offensive odour and the extracts produced for analysis are extremely complex).

Goldberg and DeLong (1973) noted that during the Kuderna-Danish evaporation step, more than one half of the absolute amount of the solutes they tested were lost, although the solute concentration increased 2 to 4 orders of magnitude. The losses for the various solutes was a function of the differing properties of the solutes. In the reduction step the analyst was simultaneously increasing contaminants and decreasing volatile solute. They also showed that large losses occurred in reducing to a volume amenable to gas chromatographic analysis. Table 2.2 shows the results of their experiments with toluene in chloroform. In order to reduce these losses, Wigilius et al. (1987) cooled the flask in an ice bath when blowing the partially reduced sample down further.

Table 2.2 Spike Recoveries and Solute Losses
(after Goldberg and DeLong 1973)

Original Volume (mL)	Final Volume (mL)	Percent Recovery
200	1.6	60.0
200	2.0	65.3
200	2.4	72.9

Junk et al. (1981) have shown that one does not have to use the traditional volume of solvent or the number of extractions to obtain efficient recoveries of the solute. Typically, the water has been extracted three times with 10% of the water volume as solvent (total solvent 30% of water volume). This volume must then be reduced to a volume amenable to gas chromatography or high performance liquid chromatography analysis (usually less than 1 mL). This concentration step has lead to several problems. Impurities in the solvent were concentrated in this step and they masked some of the compounds that are causing the taste and odour. Losses and contamination can occur because of the sample handling and transfers required. The reduction step can lead to severe losses as well as chemical changes in the chemical components because of the heat required to drive off the solvent.

The analyte recovery curves shown in Figure 2.2 are derived from the following equation by Junk et al. (1981):

$$\% E = 100D/(D + R)$$

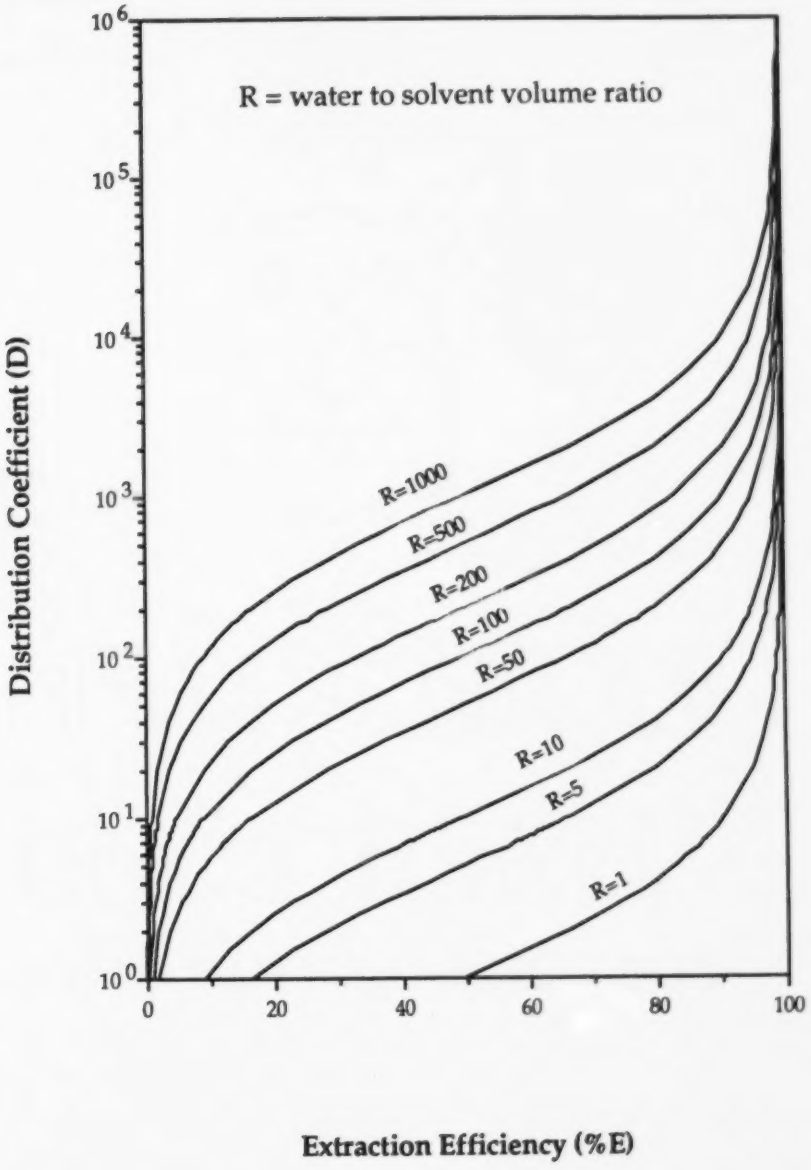
where % E = extraction efficiency

D = distribution coefficient
= concentration analyte in organic phase/concentration of analyte in the aqueous phase

R = volume ratio
= volume of water/volume of solvent

From these curves Junk et al. (1981) were able to accurately predict the recoveries at various volume ratios from one measured ratio. They also found that at R values of 100 (10 mL solvent per litre water) recoveries were ≥90% for most alcohols, alkenes and aromatics. Even at R values of 500 (2 mL solvent/L) they could recover >90% of alkanes and di, tri-chlorobenzenes. They have used volume ratios of up to 7000 but recommended 100 to 500. The drawbacks of this method were increased problems with phase separation caused by the small amount of solvent and the requirement for more vigorous or prolonged shaking to achieve equilibrium.

Figure 2.2 Liquid-Liquid Extraction Recovery Curves
(after Junk et al. 1981)



Ahnoff et al. (1974), Brownlee et al. (1984, 1988), Grob et al. (1975), Wood and Snoeyink (1977), Wigilius et al. (1987) and Slater and Blok (1983) were some of the other investigators that have made use of the micro-extraction technique. Brownlee et al., Wood and Snoeyink, and Slater and Blok have used this method for the analysis of geosmin and 2-methylisoborneol. Another micro-extraction technique was developed by Dupuy et al. (1986). They used 4 mL of a high purity vegetable oil to extract geosmin from fish and pond water with 95% recoveries from the pond water samples. The geosmin laden oil was then heated in an external inlet device at 140 °C. The carrier gas then transported the volatiles to the cool injector port (-30 °C) and then chromatographed.

Should the required compounds be resistant to the extraction, one has three options, choose another solvent with a better distribution coefficient for the compound of interest, increase number of extractions or increase the volume of solvent used. In choosing a solvent one can look at the dipole moment and the solubility of the solvent in water as an indication of the extraction efficiency. Grob et al. (1975) noted that alkanes are better solvents because of their low water solubilities (Table 2.3) although they take longer to reach equilibrium.

Table 2.3 Solvent Solubilities in Water
(after Burdick and Jackson 1984)

Solvent	Solubility (g/100 g)
Acetone	Infinitely
Methanol	Infinitely
Tetrahydrofuran	Infinitely
Methyl Ethyl Ketone	24
Ethyl Acetate	8.1
Ether	6
Dichloromethane	1.3
Chloroform	0.82
Benzene	0.18
Carbon Tetrachloride	0.08
Toluene	0.05
Cyclohexane	0.01
Pentane	virtually insoluble
Hexane	virtually insoluble

Aaberg et al. (1985) found that ethyl acetate was the preferred solvent because it was more finely distributed in the water than dichloromethane or hexane which resulted in increased rates of solute transfer. They also found that ether formed large amounts of peroxides. Although the problems with peroxide formation were not stated by the authors, they were likely due to the GC interferences (large broad peaks) and the reactivity of the peroxides which could generate artifacts.

The pH of the water, and the acid base characteristics of the compounds, prior to extraction dictates which compounds can be extracted and to what extent they are extracted. The U.S. EPA (1984) has published Method 625 in the Federal Register which stated the extraction should be carried out twice, once at pH 11 for base/neutrals and then at pH<2 for the acid extractables. Aaberg et al. (1985) showed that one extraction at pH 3 was equivalent to three extractions at pH 5 and better than eleven extractions at pH 6 in the analysis of weathered oil (which contained many acidic water soluble compounds). They used pH 3 as they found that at pH values less than this, chemical reactions occurred.

In order to reduce the volumes of solvent still further, several investigators have developed a continuous liquid-liquid extractor (CLLE) for the extraction of large volumes (20 to 200 L) of water (Goulden and Anthony 1986, Yohe et al. 1979, Ahnoff et al. 1974, Suffet et al. 1980, Goldberg and DeLong 1973). Ahnoff et al. (1974) used such an instrument to extract 200 L of water with 250 mL of cyclohexane for 0.09 to 0.31 ng/L of polychlorinated biphenyls. They also used three extractors in series to determine the efficiencies at various flow rates (81% to 95% extractor 1, 0% to 13% extractor 2 and 0% to 2% extractor 3 for flow rates of 2 to 5 L/minute). Blok et al. (1983) found their CLLE had an average extraction efficiency of 89% for 18 standards.

2.2.1.4 Concentration by Preparative GC

Many of the compounds that are associated with taste and odour problems are present at ultratrace levels (ng/L). Even at these levels, compounds such as geosmin and 2-methylisoborneol can impart objectionable flavours to treated water. Frequently, the concentration steps described in the previous sections are ineffective in providing sufficient analyte to be detected with current technology. In order to further concentrate the objectionable components of the sample, many investigators utilize the

separation capabilities of gas chromatography columns to cut certain fractions of the sample out for analysis or enrichment. This also has the added benefit of removing extraneous material that can reduce sensitivity.

Jenkins et al. (1967) used stainless steel columns (2.4 mm ID) of various lengths (1.5 m to 3 m) packed with a variety of polar and non-polar stationary phases. The columns were fitted to the gas chromatograph and placed in acetone and dry ice baths in an attempt to trap sulfur compounds obtained from cyanobacteria. Their attempts were unsuccessful as they found that they could not prevent significant losses of compounds as they were highly volatile and susceptible to easy oxidation. Consequently, they utilized distillation extraction where the receiving flask was cooled to 0°C. Medsker et al. (1968, 1969) used the same configuration to trap geosmin and 2-methylisoborneol from actinomycete and cyanobacteria cultures. Rosen et al. (1968) used preparative GC techniques to isolate geosmin from *Streptomyces griseoluteus* IM 3718 and Safferman et al. (1967) found 0.6 mg/L of geosmin in algal cultures when they isolated geosmin from *Symploca muscorum*. Daniels (1967) used traps to concentrate fractions of a sample for subsequent analysis by infrared spectroscopy. However, he could only obtain 60% trapping efficiency although good results could be obtained with sample loads as small as 2 mg. Hunt (1967) noted 6 factors that can affect collection efficiency in his description of a commercially available trapping set up that could collect as many as eight separate fractions. Efficiencies of trapping varied from 50% to 90%, depending on the compound, with an injection volume of 0.25 mL.

Sandra et al. (1980) utilized room temperature trapping to concentrate volatiles (1 m x 0.8 mm ID column) and non-volatiles (20 cm x 0.8 mm ID column). Both columns were coated with OV-101. Known odour causing compounds such as cis-3-hexenol and nonanal were concentrated on the trap which was subsequently eluted with dichloromethane and blown down with nitrogen. Recoveries were 84% to 88%. Bemmelmans and Braber (1983) used liquid nitrogen traps to concentrate bromophenols from herring extracts at the 20 to 50 µg/kg level.

Recently, more elaborate devices for the fractionation of components have been developed by a number of investigators. Wassgren et al. (1984) used a revolving fraction collector cooled with dry ice and ethanol to trap volatile components with recoveries of 50% to 65%. He used 60 mm x 1.6

mm ID PTFE tubes to trap volatile compounds while simultaneously obtaining an FID trace. Roeraade et al. (1986) developed a particularly elegant instrument with a manifold so that a number of fractions could be collected on capillary columns. The 2 m x 0.6 mm ID columns were cooled in dry ice/ethanol baths attached to the manifold with shrink wrap PTFE or capillary micro-connectors. This instrument was microprocessor controlled to facilitate automated concentration of a large number of injections. Recoveries were deemed acceptable although they never exceeded 80%. Claude and Tabacchi (1988) used two columns in parallel with a solenoid switching valve. When the compound of interest was eluting, the valve would switch over to the collection column for trace enrichment.

In their attempts to determine the efficiencies of concentration methods, Lundgren et al. (1988b) used preparative gas chromatography techniques to fractionate water extracts from polluted rivers, oligotrophic lakes and disinfected drinking water (ozone and chlorine). They demonstrated the utility of this method by re-dissolving the fractions in odour free water to determine the offending fraction, and subsequently the offending compounds.

2.2.2 Sensory Characterization Methods

Zoeteman et al. (1980) discussed the measurement of chemicals or tastes for the indication of water quality. They recommended using taste and odour assessments as 'only in exceptional cases will the measurement of a few chemicals be representative for the occurrence of taste problems'. The chemical analysis becomes more complex when one considers that any given sample may contain thousands of different compounds.

2.2.2.1 Threshold Odour Number

The Threshold Odour Number (TON) is defined as the greatest dilution of a sample that retains a definitely perceptible odour by an individual or panel. By definition, the TON at the odour threshold concentration for a given chemical is zero as any dilution will reduce the odour to non-perceptible levels for 50% of the panel.

Five different volumes of sample are added to 500 mL Erlenmeyer flasks which contain sufficient odour free water to make a final volume of 200 mL. Several blanks containing 200 mL of odour free water are also

prepared and the samples presented to a panel of five or more persons, in random order. The samples are shaken and the vapour sniffed by each member of the panel and the odour or lack of odour recorded. The TON value is calculated according to the following formula.

$$TON = (A + B)/A \qquad \text{where} \qquad A = \text{mL of sample}, \; B = \text{mL odour free water}$$

A similar test, the Odour Intensity Index (OII) is defined as the number of times the concentration of an original sample is halved by the addition of odour free water to obtain the least definitely perceptible odour. TON is related to the OII in the following manner.

$$TON = 2^{OII} \quad \text{or as sometimes written} \quad \log TON = OII \log 2$$

The TON has been widely used in the water treatment industry as a method to quantify the intensity of an odour event. Lind et al. (1988) has used this method to note increases in odour in reservoir water caused by actinomycetes. In their experiments with ozone, Lundgren et al. (1988a) showed that the TON increased as the ozone dose increased and Amoore (1986) has used it extensively to determine specific anosmia and odour threshold concentration values. Anselme et al. (1988) showed that the intensity of the fruity odour produced by ozonation was directly proportional to the log of the concentration of the C_6 to C_{12} aldehydes present. TON values of 3 are used to set secondary (aesthetic) maximum contaminant levels in the United States and Europe (Mallevialle et al. 1987). In 1973 the Metropolitan Water District of Southern California (MWDSC) had TON values of over 200 in their water after a cyanobacterial bloom in their reservoir (Spitzer 1976). After this event they began a routine monitoring program of the reservoir using TON that determined which of the intakes on their multi-leveled intake structure should be used. The City of Chicago used the TON to determine when to apply powdered activated carbon (TON > 1.5, Spitzer, 1976).

Jardine (1988) used the TON method to evaluate the raw and treated water in the City of Edmonton during the spring of 1988. She found that the five panel members could effectively track odour events although the

panelists varied considerably in their individual sensitivity. Jardine also noted that samples giving relatively high TON's of 40 to 60, were not objectionable to the public. This implied that sensory evaluation of the raw and treated water can be used as a monitoring tool for the operation of water treatment plants as it may identify problems before they are perceived by most members of the public.

Krasner et al. (1985), Mallevialle et al. (1987) and others have noted that there are disadvantages or flaws in the TON method. First, it does not distinguish between objectionable and acceptable or tolerable odours (e.g. chlorine). An extremely objectionable odour may give a low TON and an acceptable one a high TON. Mallevialle et al. (1987) have noted that: 'TON itself does not correlate well with the level of acceptability of a particular water by the consuming public'. Another problem has been that by diluting the sample the character of the odour may be changed. Persson (1980b) showed that at high concentrations, 2-methylisoborneol had a camphor odour whereas at low concentrations, it was distinctly earthy/musty. In practice, the TON method is extremely tedious because of the large number of dilutions and duplicates (one for each panel member) required to characterize a single sample of water. McGuire (1983) noted that earthy musty odours tend to be masked by other odours especially when heated to 40°C to 60°C as called for by this method. He also found that odours were being generated when the samples were heated.

2.2.2.2 Flavour Profile Analysis

The Flavour Profile Analysis Method (FPA) was implemented in the water treatment industry to overcome some of the inherent problems of the TON method. It was originally developed in the food industry by Cairncross and Sjostrom (1950) and implemented at the Metropolitan Water District of Southern California (MWDSC) by Krasner et al. (1985). The method has recently been included as a proposed method in the 18th Edition of Standard Methods (APHA, AWWA, WEF, 1992). Persson (1988b) has stated that the development and implementation of the FPA method has been the major advance in the study of odour problems in the water treatment industry. Krasner (1985) has found that the intensity scale correlated very well with 2-methylisoborneol concentrations in a semi-logarithmic calibration plot. This confirmed the Weber-Fechner Law which stated that the intensity of an

odour is directly proportional to the logarithm of its concentration. Subsequent chemical investigations of authentic water events confirmed that the dose-response generated by the FPA method was indeed accurate. Bousquet et al. (1983) performed a statistical evaluation of FPA using a blind test method which indicated the utility of the method for water treatment plants. Meng et al. (1991) correlated chemical analysis to FPA data using Principle Component Factor Analysis.

To perform an FPA analysis, a panel must be assembled and tested to ensure a minimum sensitivity in all members. Bartels et al. (1987) described the multi-step testing and training procedure. They used the procedure to train 16 university students and found that they became adept at the method after a few training sessions. Bosquet et al. (1983) have noted that their investigations into the FPA method have shown that periodic retraining or calibrations are required. Several researchers have made use of the University of Pennsylvania's Smell Identification Test (UPSIT) developed by Doty et al. (1984) which can be used to screen potential panel members (Bartels et al. 1986a, Engen et al. 1987). The test uses microencapsulated odours which the individual panelists scratch and sniff. Their results will indicate any specific anosmia in any panelist.

In an FPA session, samples are presented to each member of the panel simultaneously and the samples are evaluated using two or three short sniffs. The samples can also be tasted, using a slightly different procedure, but Amoore (1986) notes that much of the 'taste' in water is actually the odour that is perceived as the water is swallowed. Each panel member records the perceived intensity as measured on a seven point scale as shown in Table 2.4 with an odour descriptor.

The results are then collected by the leader and any differences between members are resolved. The final FPA value is recorded as the predominant descriptor and the average of the intensity scores.

Burlingame et al. (1986) noted that the FPA method can be used to analyze a large number of samples and has been used to locate the cyanobacterial origin of geosmin in a river. Krasner et al. (1989) tracked fishy odours and those caused by dimethyl polysulfides in the reservoir and plant. Bartels et al. (1986a, 1986b) noted that the FPA method has been used successfully at the Metropolitan Water District of Southern California (MWDSC), Philadelphia Suburban Water Company, Philadelphia Water

Department and Lyonnaise des Eaux since 1984. Lyonnaise des Eaux used the method to monitor its process and adjust it accordingly. When the MWDSC switched from free chlorine to chloramines, Krasner et al. (1985b) used the FPA method to track the formation of nitrogen trichloride because its OTC was an order of magnitude lower than the analytical detection limit (0.02 mg/L vs 0.2 mg/L).

Table 2.4 FPA Intensity Scale
(after Mallevialle and Suffet 1987)

Odour Descriptor	Intensity
Threshold	0.25
Very Slight	0.5
Slight	1.0
Slight to Moderate	1.5
Moderate	2.0
Moderate to Strong	2.5
Strong	3.0

2.2.2.3 Chromatographic Sniffing

Many odour causing compounds have odour thresholds below their analytical detection limits which can make isolation extremely difficult. In order to overcome this, many researchers have utilized sensory gas chromatograph techniques to isolate portions of the chromatograms that are responsible for odour problems. Jenkins et al. (1967), Medsker et al. (1968, 1969), Bemmelmans et al. (1983), Berglind et al. (1983a), Lundgren et al. (1988a) and Veijanen et al. (1983) have used this technique in the analysis of off-flavours in water. McGorrin et al. (1987) has used this technique to determine the cause of a musty odour associated with plastic packaging. Sandra et al. (1980) used GC sniffing for plant material extracts in order to identify aldehydes and alcohols. The naranjilla fruit has a very distinct odour and Brunke et al. (1989) generated odourgrams and identified aldehydes, alcohols, esters, acids and lactones but found that esters of butanoic acid and ethyl acetate were the principle components that determined its odour. Berglund et al. (1982) identified C_{5-6} aldehydes, 2-butanone, o-xylene and C_3 alkyl

benzenes in the odourgrams of air sample extracts collected from new buildings.

Once the odorous sections of the chromatograms have been isolated, they may be concentrated for further analysis by mass spectrometry. Alternatively, the odour descriptors and retention time can be compared to known taste and odour causing compounds for identification.

Jenkins et al. (1967) noted that GC sniffing has been used extensively in the perfume industry in their paper on the malodorous sulfur compounds associated with cyanobacterial blooms in California reservoirs (mercaptans and dimethyl polysulfides). Medsker et al. (1968, 1969) isolated geosmin and 2-methylisoborneol from cyanobacterial and actinomycete extracts. More recently, some investigators have split the flow on the GC to obtain FID chromatograms concurrently with the odourgrams (Sandra et al. 1980, Berglund et al. 1982, Veijanen et al. 1983, Bemmelmans and Braber 1983, Berglind et al. 1983a, McGorrin et al. 1987, Brunke et al. 1989). Lundgren et al. (1988) did not split the sample as it was difficult to control the split ratio and the concentration of the odorous components was so low that any splitting may have led to lost peaks.

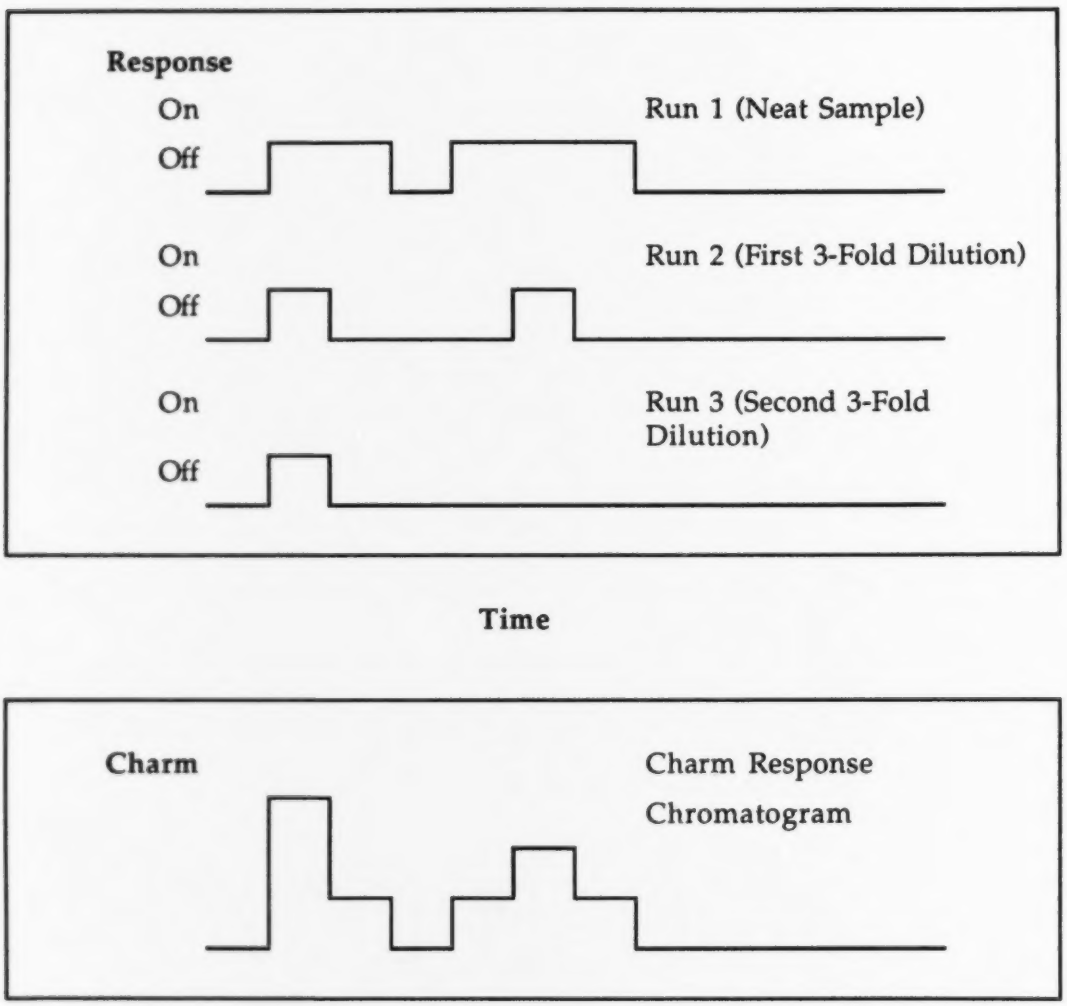
Khiari et al. (1992) used two columns, one for the FID analysis and one for the sniffing analysis. The sniffing injection was delayed twenty seconds so that the sniffing could begin after a peak was noticed eluting on the FID chromatogram. This could lead to lost peaks as Bemmelmans et al. (1983) noted that the FID traces of tainted and untainted herring extracts were similar in the regions of intense odour indicating that the odorous compounds were present in trace concentrations. Savenhed et al. (1986) also showed that the most intense odours were not the most significant peaks in a chromatogram. Most often they were associated with the background or grass of the chromatogram traces. Berglund et al. (1982) compared their perceptio-olfactograms to FID chromatograms and found little or no correlation indicating that the sensitivity of the FID is insufficient to identify the odorous components of the sample.

Several investigators (Berglind et al. 1983a, Brunke et al. 1989, Veijanen et al. 1983, Khiari et al. 1992) added a humidified air stream to the capillary column effluent as the dry hot air emanating from the column tended to dry out the mucous membranes of the human sensors. Brunke et al. (1989)

coupled the humidified GC effluent to a mask that the sensor wore so as not to miss any peaks.

In an attempt to quantify the sniffing procedure, Zurer (1987) reported what the developers termed the charm response chromatogram (Figure 2.3). In this method the cooled and humidified gas stream emanating from the GC column was sniffed. The time and duration of all odours were recorded by the depression of a switch. The sample was then diluted by one third, sniffed, diluted by one third and sniffed again. The sum of all odourgrams was calculated to give the charm response chromatogram.

Figure 2.3 Charm Chromatogram
(after Zurer 1987)



3.0 Research Objectives

After conducting a review of the literature, and a more specific review of Edmonton's problem, a research plan was developed that would utilize chemical and sensory techniques to identify the odours components of Edmonton's raw and finished water. The plan had the following objectives.

1. To develop a procedure for extracting the adsorbed organics from granular activated carbon that had been exposed to raw or treated water during a major taste and odour event.

2. To employ gas chromatographic sniffing procedures to identify the offending odours in water by retention time and odour description.

3. To develop preparative gas chromatographic techniques to concentrate those components identified in objective 2.

4. To utilize gas chromatography-mass spectrometry to identify compounds in the samples and concentrated extracts generated in objective 3.

5. To evaluate the effectiveness of the Alberta Environmental Centre's pilot plant process streams at removing or avoiding the production of odour agents from the raw water.

4.0 Materials and Methods Development

The granular activated carbon used for this work was prepared by the City of Edmonton in the spring of 1989 as part of their strategy to determine the cause(s) of their recurring taste and odour problems. The procedure used to load the carbon is described in Section 4.2. This carbon was provided to the University of Alberta in the summer of 1990 and constituted the starting point for this research. This was viewed as a unique opportunity because taste and odour episodes are transient. In particular, there has not been a substantive spring taste and odour event that would compare with the 1989 event (i.e. from 1990 to 1994).

In order to ensure no cross contamination of samples, all used (i.e. dirty) glassware was rinsed with the solvent used for that portion of the experiment prior to washing in a Miele® dishwasher with Heikol® detergent at 85°C. This machine allowed a phosphoric acid rinse and two distilled water rinses at 85°C. The glassware was then dried in a dedicated glassware oven at 65°C. All vials, fingers for Soxhleting and round bottom flasks were also soaked in a chromic acid bath overnight prior to washing in the dishwasher. Prior to use, the cleaned glassware was rinsed twice with the solvent to be used.

4.1 Reagents

4.1.1 Solvents

Table 4.1 lists the five solvents that were used to extract the granular activated carbon along with their properties. Chriswell et al. (1977) found that various solvent combinations were good for some compounds and bad for others confirming that there is no universal solvent that is applicable to all compounds and matrices. The requirements of the solvents were that they had to be relatively volatile (i.e. low boilers), have a range of polarities and be readily available. These solvents were chosen to provide a wide range of polarities from the non-polar hexane to the highly polar methanol. By using the range of solvent polarities it was hoped that most GAC adsorbable components in the water could be extracted from the GAC and pre-separated prior to GC analysis, thereby facilitating identification.

Preliminary tests on the solvents indicated that for dichloromethane, the pesticide grade from Fisher Scientific was superior to triply distilled ACS

BDH assured grade available in 20 litre cans. This was determined by concentrating 500 mL of the solvent to 2 mL via Kuderna Danish evaporation. The samples were further reduced to approximately 200 µL with a gentle stream of nitrogen. The GC-FID traces of the various grades of solvents were then compared and the superiority of the pesticide grade solvents noted.

Table 4.1 Solvent Properties

Solvent	Molecular Weight	Dielectric Constant*	Boiling Point (°C)	Density (g/mL)	Solubility in Water	Relative Polarity
Hexanes	86.18	1.89	69.0	0.6603	insoluble	non-polar
Ethyl Acetate	88.12	6.02	77.1	0.9003	soluble	non-polar
Dichloromethane	84.93	9.08	40.0	1.3266	slightly	intermediate
Acetone	58.08	20.7	56.2	0.7899	infinitely	polar
Methanol	32.04	32.63	65.0	0.7914	infinitely	very polar

* - The dielectric constant is a measure of relative polarity

During the tests on the various grades of acetone, it was noticed that the final concentrate was highly coloured (yellow) and gave a very dirty FID trace. The relative complexity of the trace was found to be a function of the Kuderna Danish bath temperature with higher temperatures producing more artifacts. The temperature of the bath, as well as the subsequent Soxhlet extraction temperatures, were therefore adjusted to provide sufficient heat to just volatilize the solvents.

As a result of the solvent tests, pesticide grade solvents were used as received for the remainder of the experiments. However, further testing of the solvents during the extraction procedures demonstrated the variable quality of different batches of solvents which was confirmed by another lab (Skinner 1989).

4.1.2 Chemicals

Table 4.2 lists the chemicals used, their purities and their suppliers. All of these chemicals were used as received.

Anhydrous sodium sulphate (Na_2SO_4) was obtained from Fisher Scientific in 10 kg lots and used to remove any residual water from the solvent extracts. The Na_2SO_4 was Soxhlet extracted in pesticide grade

dichloromethane for 24 hours, dried in a fume hood then baked at 550 °C overnight, cooled and subsequently stored in a desiccator.

Glass wool used in the Soxhlet apparatus and filtering steps was Soxhlet extracted for 24 hours with pesticide grade dichloromethane. The glass wool was then allowed to dry in a fume hood and then stored in a two litre beaker covered with a watch glass until required.

Table 4.2 Chemical Properties of Odorous Chemicals and Standards

Chemical Name	CAS Registry #	MW (g/mole)	Boiling Point (°C)	Melting Point (°C)	Density (g/mL)
cis-3-hexenol	[544-12-7]	100.16	156-157		0.846
1-chlorohexane	]544-10-5]	120.62	133-134		0.879
1-chlorooctane	[111-85-3]	148.68	183		0.875
ß-cyclocitral	[432-25-7]	152.1			
2-isopropyl-3-methoxy pyrazine	[25773-40-4]	152.2			0.996
2-isobutyl-3-methoxy pyrazine	[24683-00-9]	166.22			0.99
2-methylisoborneol	[28405-88-1]endo [2371-42-8]exo	168			
1-chlorodecane	[1002-69-3]	176.73	223	-34	0.868
2,6-dichloroanisole	[1984-65-2]	177.03		10.1	1.291
geosmin	[19700-21-1]	182.31	270		
1-chlorododecane	[112-52-7]	204.79	130		0.87
2,3,6-trichloroanisole	[50375-10-5]	211.48		44-46	
2,4,6-trichloroanisole	[87-40-1]	211.48	132	60-62	
1-chlorotetradecane	[2425-54-9]	232.84	139-142		0.859
1-chlorohexadecane	[4860-03-1]	260.89	149		0.865
1-chlorooctadecane	[3386-33-2]	288.95	157-158		0.849

*All chemicals obtained from Aldrich except for ß-cyclocitral (Sigma), 1-chlorododecane (Eastman Kodak), geosmin and 2-methylisoborneol (Raylo Chemicals)

4.2 Organic Adsorption onto Granular Activated Carbon

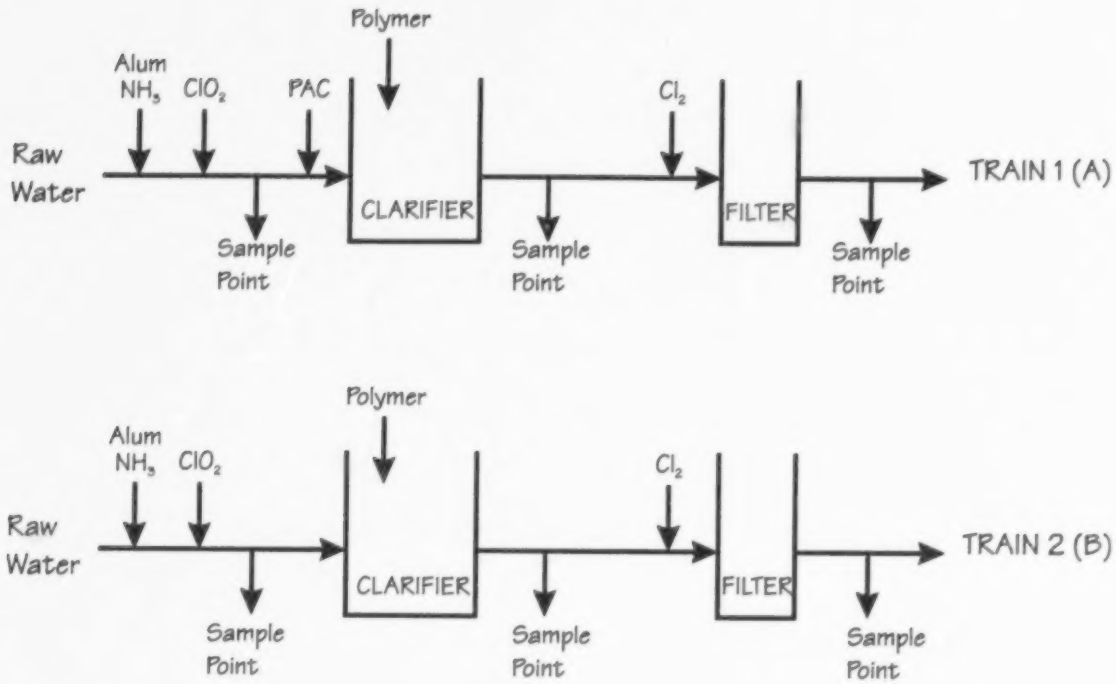
Filtrasorb 300, a granular activated carbon (GAC), was obtained from Calgon Carbon and washed with distilled water to remove any fine material. Approximately 200 grams (on a dry weight basis) of this wetted carbon were

packed into a column and approximately 2000 litres of water were passed over it during a twenty-four hour period.

The raw and treated water originated from the North Saskatchewan River at the City of Edmonton's EL Smith Water Treatment Plant located approximately 17 kilometers west (upstream) of the city centre. The water passed through the granular activated carbon columns was generated by Alberta Environment's mobile water treatment plant. These columns, approximately 30 cm by 4 cm ID, were constructed of stainless steel. Glass wool plugs and stainless steel screens held the carbon in place during the adsorption phase. Several streams were used that included a raw water and two treated water processes, one of which, stream A, utilized powdered activated carbon (PAC). These streams are shown in Figure 4.1. The two treated streams consisted of flocculation/coagulation with aluminum sulfate (alum), primary disinfection with chlorine dioxide (ClO_2), clarification with polymer addition, secondary disinfection with chloramines followed by filtration. In the second stream, PAC was added just prior to clarification. After the 24 hour period had passed, the carbon was recovered from the columns and placed in wide mouthed 1.5 litre jars with Teflon® liners. After completion of the experimentation the carbon samples were transported to the Alberta Environment laboratories in Vegreville, Alberta and frozen. Just prior to extraction the GAC samples were taken to the University of Alberta and stored in a freezer until extracted.

To determine the efficiency of the GAC adsorption, recoveries for a variety of compounds were conducted. One litre of methanol containing a cocktail of odorous compounds was passed over virgin and preloaded GAC (from the City of Edmonton pilot plant, April 1/2) contained in a column. The effluent from this column was collected and analyzed for the target compounds and the GAC Soxhlet extracted with pentane and dichloromethane as described below.

Figure 4.1 Mobile Water Treatment Plant Process Streams



4.3 Extraction and Concentration Procedures

After the frozen GAC was removed from the freezer and thawed, it was fully mixed to ensure a homogeneous sample was obtained. The protocol used to extract the GAC is contained in Figure 4.2. A 40 gram sample was then placed on top of a glass wool plug in the Soxhlet apparatus. At the same time, 3 smaller aliquots of approximately 0.8 grams each were placed in baked and weighed 40 mL vials and put in an oven at 65 °C overnight to determine the moisture contents of the GAC samples. The round bottom flask, containing 200 mL of solvent, was then attached and the heating mantle set so as to achieve a gentle reflux using chromic acid washed glass beads. As the solvent volatilized, it passed through a large tube on the outside of the apparatus to a condensor where it liquified and came in contact with the GAC (Figure 4.3). The apparatus filled with solvent until the level rose above the top of a smaller tube which then began to drain and siphon out the solvent. Solute free solvent was then re-evaporated and re-condensed to successively extract the carbon approximately 12 times per hour. After 20 hours the heating mantle was shut off and the apparatus allowed to cool with the remaining solvent in the apparatus drained to the round bottom flask. This flask was then exchanged for another that contained the next, more polar solvent and the process repeated. The order of the solvent extraction was hexanes ethyl acetate, dichloromethane, acetone and finally methanol.

The solvent extracts were then passed over anhydrous sodium sulphate to remove any water present and into the Kuderna Danish apparatus (Figure 4.4) which was placed in a water bath. The temperature of the water bath was increased until the solvent just began to distill over. When the sample was reduced to approximately 8 mL, the apparatus was removed from the bath and allowed to cool. Clean 40 mL vials were then rinsed three times with fresh solvent and the samples transferred into them. The entire apparatus was then rinsed three times with the appropriate solvent which was also transferred to the 40 mL vial.

This sample (approximately 12 mL) was then further reduced under a gentle stream of nitrogen (prepurified grade) to approximately 1 mL and was transferred to a 3.5 mL vial. The sample was stored this way until just prior to analysis where it was reduced to a final volume of approximately 250 µL by a gentle stream of nitrogen.

Figure 4.2 GAC Extraction Protocol

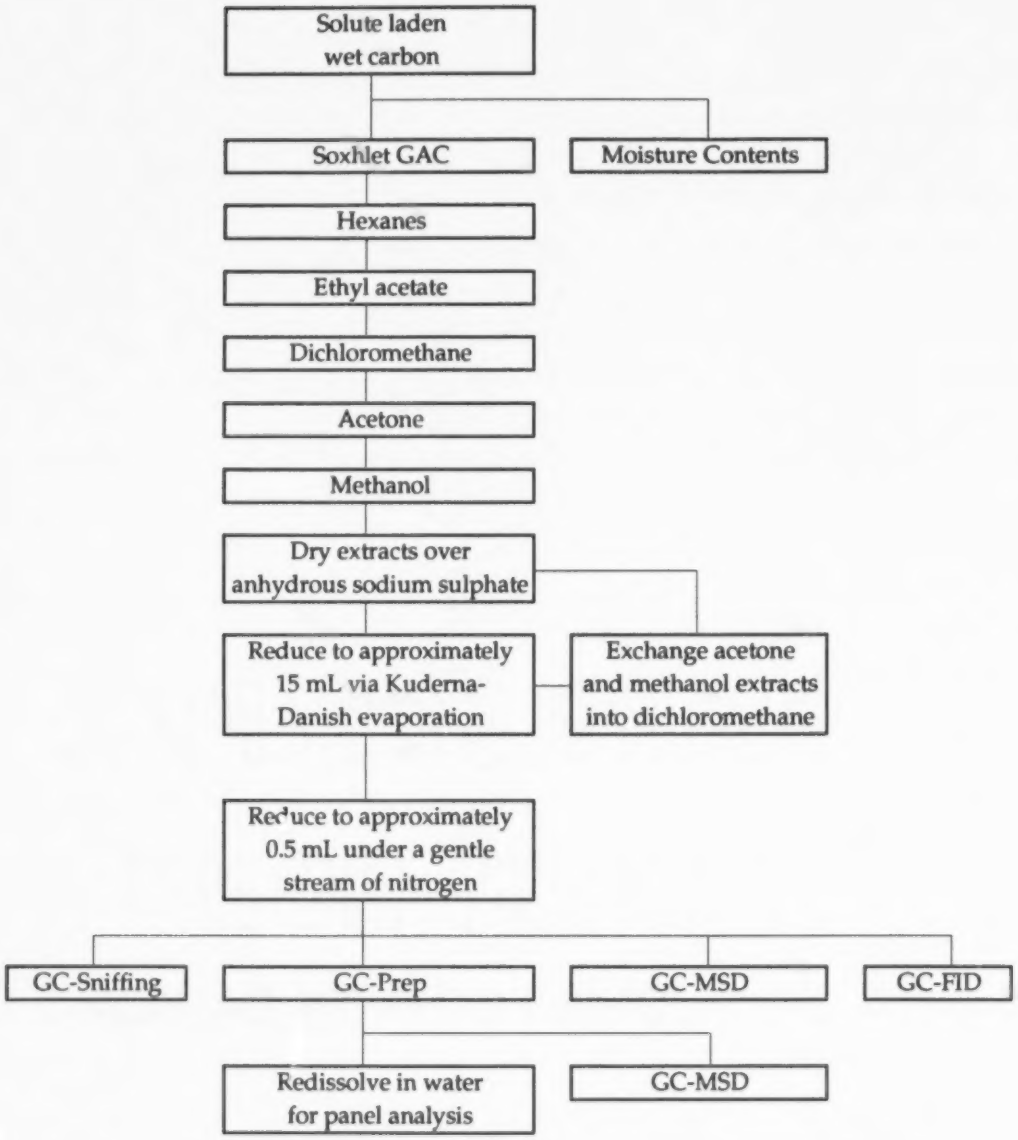


Figure 4.3 Soxhlet Apparatus

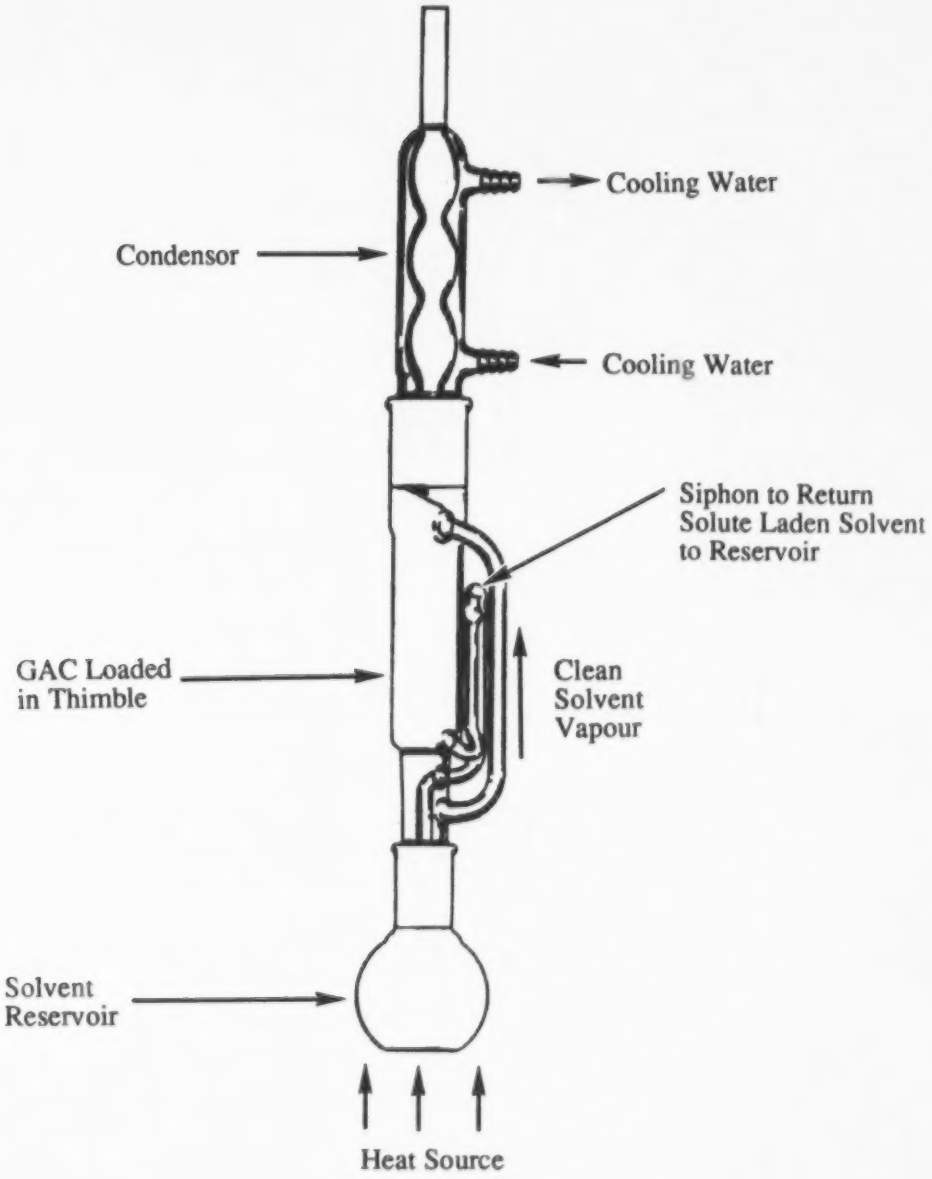
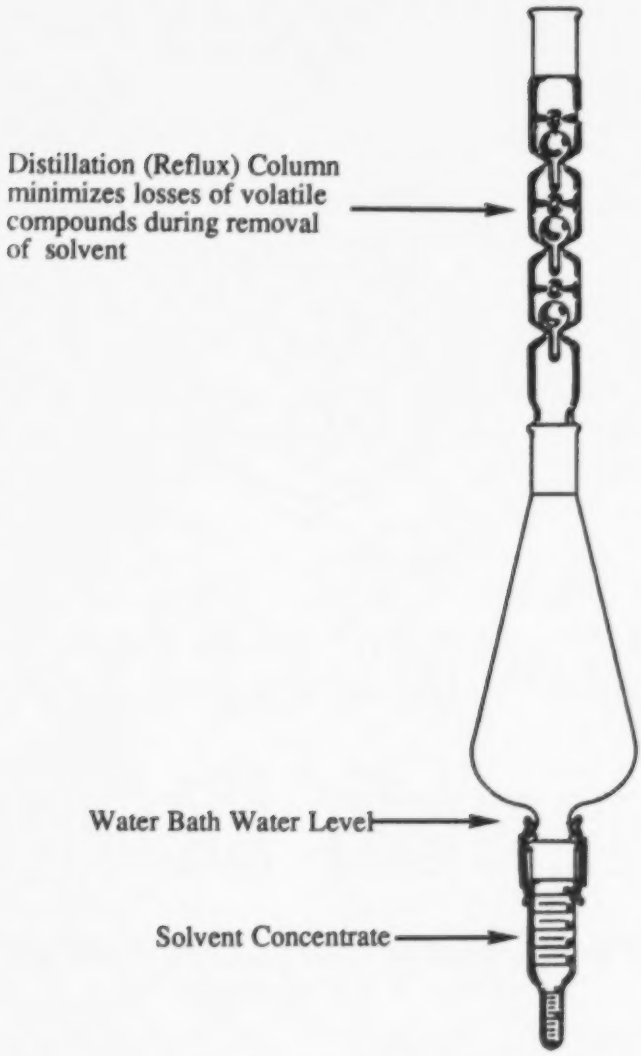


Figure 4.4 Kuderna Danish Apparatus

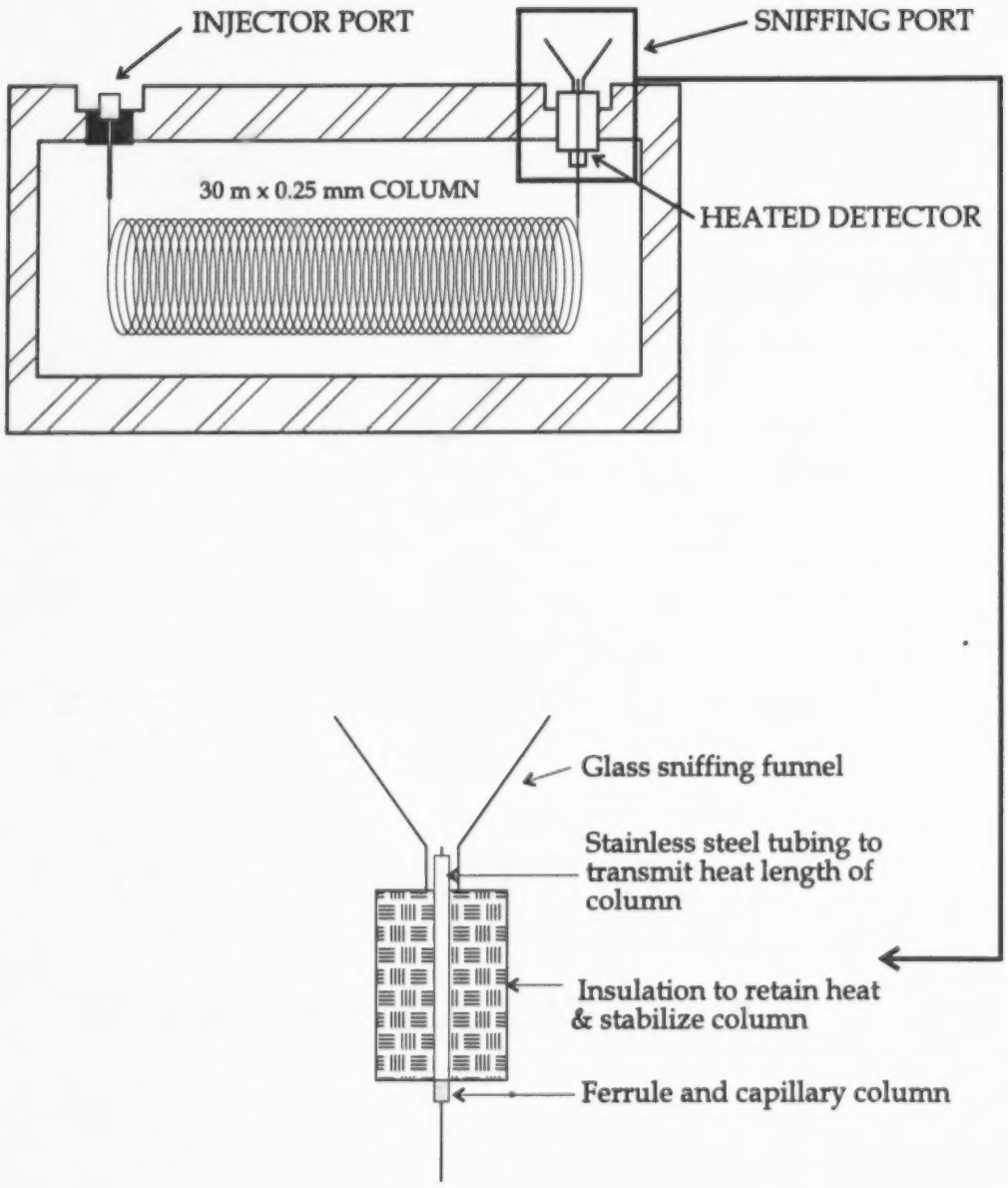


4.4 Sniffing Procedures

A Hewlett-Packard HP-5890 gas chromatograph (GC) was used for all of the sniffing experiments. The GC was modified by removing the flame ionization detector (FID) and the flame jet and pushing the column outlet up approximately 10 cm (Figure 4.5). A 7 cm length of stainless steel tubing was then placed over the column to transfer heat up from the heating block. This was done so as to prevent the condensation of the components in the capillary column or significantly impact the retention times. Insulation material was then packed into the space between the tubing and FID block to stabilize the column as well as to retain heat. The sniffing apparatus was completed with the addition of a glass funnel over the column/tubing with approximately 0.5 cm of it protruding into the funnel. Between runs the funnel was washed with pesticide grade acetone and dried in an oven to prevent carry over of odours.

Runs were completed using the GC parameters and conditions listed in the next section. As the odorous components of the sample eluted from the column the time, intensity as well as an odour descriptor were recorded. Because of the frequency of odour elution or extremely odd odours, some chemicals were not given an odour descriptor. These components were given the label 'dd' which stands for 'defies description'.

Figure 4.5 GC Sniffing Configuration


INJECTOR PORT
SNIFFING PORT
30 m x 0.25 mm COLUMN
HEATED DETECTOR
Glass sniffing funnel
Stainless steel tubing to transmit heat length of column
Insulation to retain heat & stabilize column
Ferrule and capillary column

4.5 Gas Chromatography and Mass Spectrometry Conditions

Flame ionization detector chromatograms, sniffing odourgrams and preparative GC work were all performed on an HP 5890 GC in splitless mode. Another GC, an HP 5890 Series II was fitted with an Hewlett-Packard mass selective detector (HP MSD 5971) that was used for all mass spectrometry analysis.

Three columns were used in this research and Table 4.3 summarizes their dimensions, phases and relative polarities. The majority of the analyses were performed on a DB-1 column (J&W Scientific) with a 60 m column being purchased and split into two 30 m columns. This was done to obtain two columns with similar properties such as coating thickness which would impact the retention times. One of these columns was permanently placed in the GC-MSD with the other used for the GC preparative work, FID traces and the majority of the sniffing analyses. Tables 4.4 and 4.5 list the GC conditions and gas flows used.

For the GC-MSD experiments the mass spectrum was routinely scanned from 35 amu to 350 amu as the specific compounds causing the taste and odour were not known. Once several suspected agents were found, the GC-MSD was run in the selected ion monitoring mode where it only scanned a limited number of diagnostic peaks. For geosmin these peaks were 112, 125, 126, 149, 167, and 182 and for 2-methylisoborneol they were 95, 108, 150 and 168.

A series of 1-chloroalkanes (C_6 to C_{18}) were used to determine the relative retention times of odorous components and to quantitate inter GC differences due to flow rates, column differences and temperature changes. The chloroalkanes also provided a check on the performance of the GC with respect to sensitivity and retention times.

Table 4.3 GC Column Properties

Column	Stationary Phase	Film Thickness (μm)	Dimensions	Supplier
DB-1 nonpolar	dimethyl-polysiloxane	0.25	30 m x 0.252 mm	J&W Scientific
SPB-20 low polarity	20% diphenyl 80% dimethyl-polysiloxane	0.25	30 m x 0.25 mm	Supelco
DB-WAX polar	polyethylene glycol	0.5	30 m x 0.317 mm	J&W Scientific

Table 4.4 Gas Chromatograph Gas Supply

Gas Type	Flow Rate (mL/min)	Grade
Helium (carrier)	1	Zero Gas
Hydrogen (flame)	40	Prepurified
Nitrogen (make-up)	30	Prepurified
Air (flame)	270	Zero Gas

Table 4.5 Gas Chromatograph Operating Parameters

Chromatograph Element	Temperature or Program
Oven	35 - (5 min) - 5°/min - 290 (5 min)
Injector	150 (later 250)
Detector - FID	300
Detector - MSD	250

5.0 Results

Table 5.1 lists the samples used for the experiments and the analyses performed upon them. In addition, raw, treated and treated with PAC, granular activated carbon samples from April 1/2, 2/3, 7/8, 8/9, 9/10, 10/11, and 11/12 were extracted with 5 different solvents providing an additional 105 extracts that could have been analyzed if necessary. The tabulated results of the sniffing experiments (odourgrams) on the raw and treated samples are contained in Appendix B. Graphical comparisons of the sniffing experiments for the three different water streams on April 4/5 1989 are presented in Figure 5.1 (hexane extracts), Figure 5.2 (dichloromethane extracts) and Figure 5.3 (ethyl acetate extracts). Similar graphical comparisons for April 5/6 and 6/7 1989 are contained in Appendix C.

Table 5.2 presents the results of the retention time study for geosmin and 2-methylisoborneol on different columns and Table 5.3 presents the results of the model compound recovery study. Figures 5.4 to 5.16 present the mass spectral data for identified compounds.

The methodology, results and discussion of the preparative gas chromatography experiments of this research is contained in Appendix D.

Table 5.1 Sample Analyses Summary

Sample Date and Location	Number of Extractions	Number of Chromatograms	Number of Mass Spectral Analyses
April 4/5 Raw	5	5	5
April 4/5 Treated	5	5	5
April 4/5 Treated+PAC	5	5	5
April 5/6 Raw	5	5	5
April 5/6 Treated	5	5	5
April 5/6 Treated+PAC	5	5	5
April 6/7 Raw	5	5	5
April 6/7 Treated	5	5	5
April 6/7 Treated+PAC	5	5	5

Table 5.2 Retention Times of Geosmin and 2-Methylisoborneol on Different Columns as Measured by GC-FID and GC-Sniffing

Chemical	DB-1		SPB-20	DB-WAX	
	FID	Sniff	FID	FID	Sniff
1-ClC6	11.87		12.09	8.32	
1-ClC8	19.83		20.01	15.35	
1-ClC10	26.58		26.72	21.64	
1-ClC12	32.43		32.57	27.18	
1-ClC14	37.62		37.78	32.14	
1-ClC16	42.27		42.48	36.64	
1-ClC18	46.50		46.75	40.78	
geosmin standard	31.17	31.19	31.89	31.42	31.07
musty sample*		31.21			31.04
2-MIB standard	24.39	24.33	24.80	25.62	25.17
menthol sample*		24.30			25.17

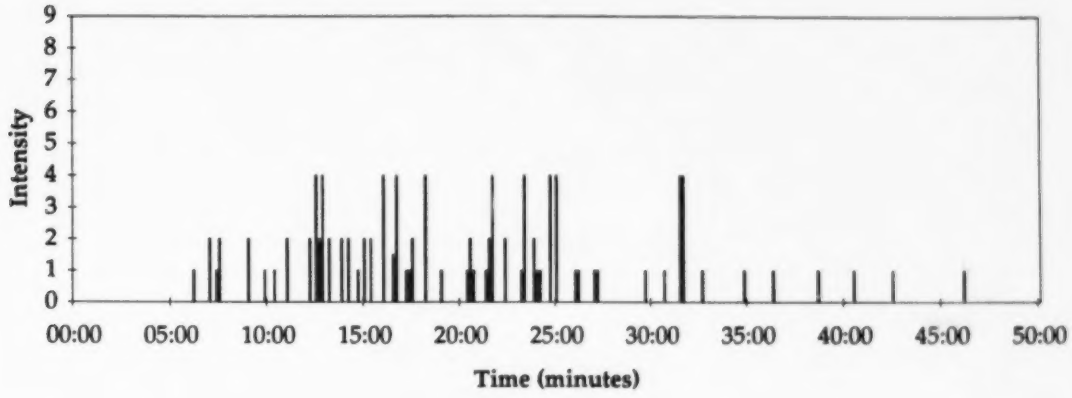
* - sample used for tests was hexane extract from 5/6 April 1989

Table 5.3 Recoveries of Model Compounds from Activated Carbon

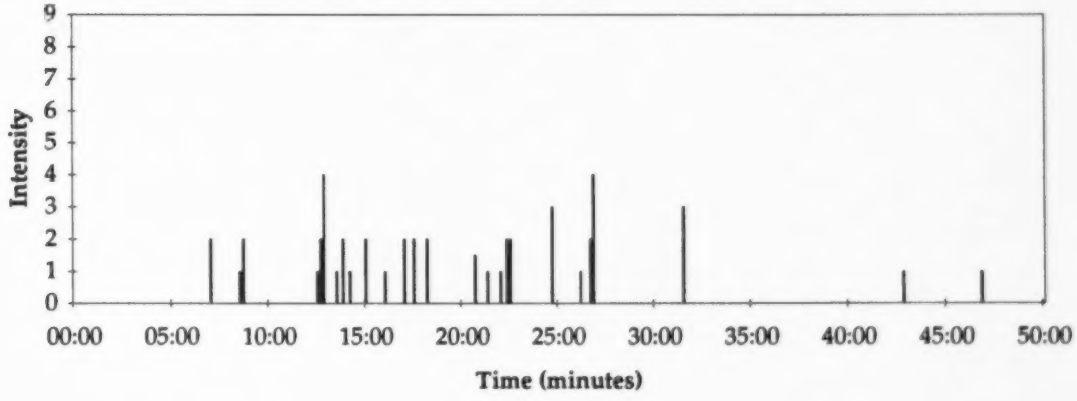
Model Compound	Percent Recovery	
	Preloaded Carbon	Virgin Carbon
benzaldehyde	4	83
geosmin	86	111
2-isopropyl-3-methoxy pyrazine	100	130
2-isobutyl-3-methoxy pyrazine	82	101
2-methylisoborneol	31	112
phenylacetaldehyde	93	120
2,4,6-trichloroanisole	31	20
2,3,6-trichloroanisole	60	33

Figure 5.1 Odourgrams of the Hexane Extracts from 4/5 April 1989

Raw



Treated without PAC



Treated with PAC

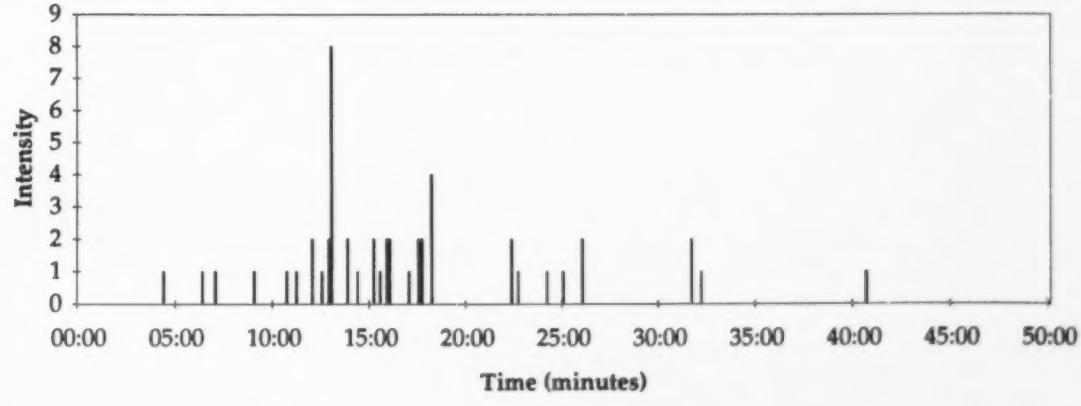
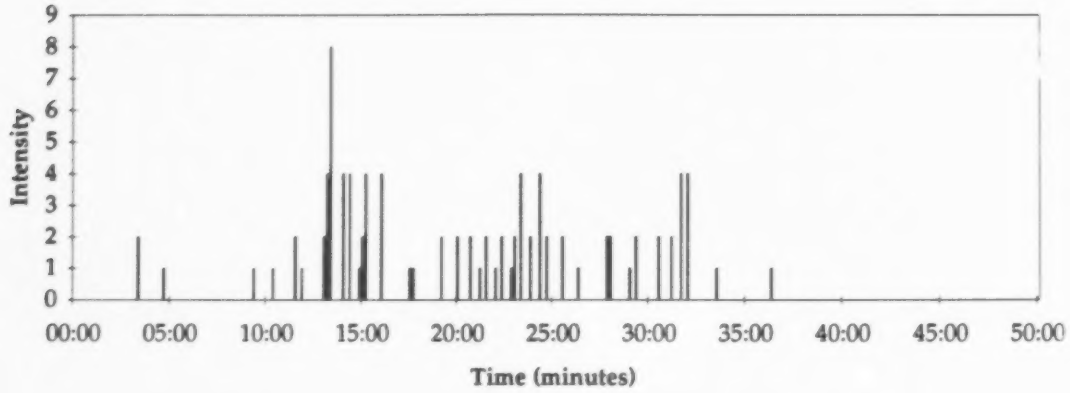
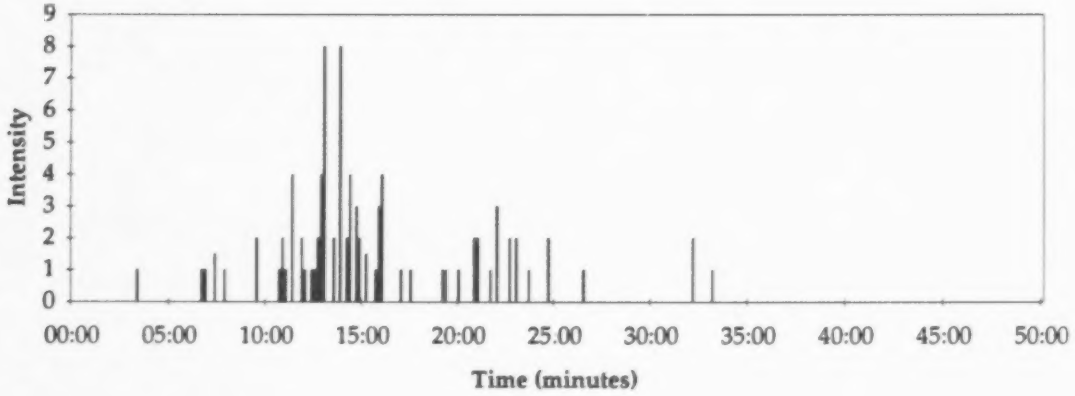


Figure 5.2 Odourgrams of the Ethyl Acetate Extracts from 4/5 April 1989

Raw



Treated without PAC



Treated with PAC

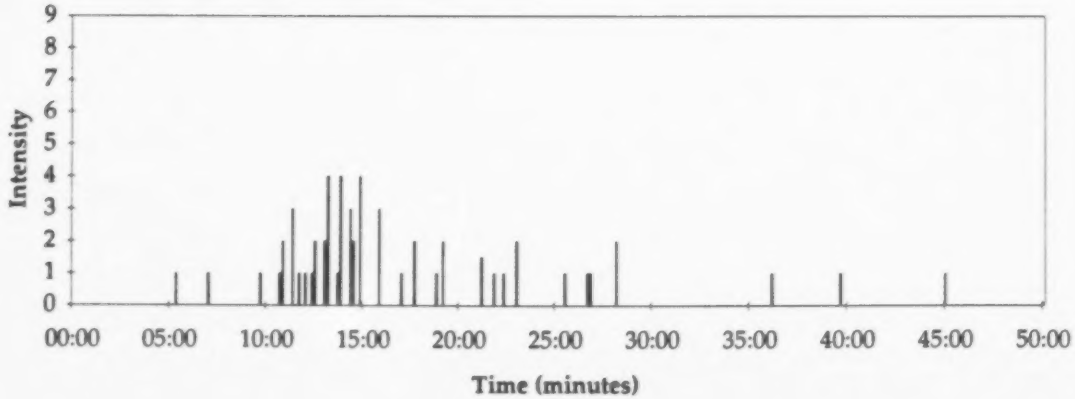
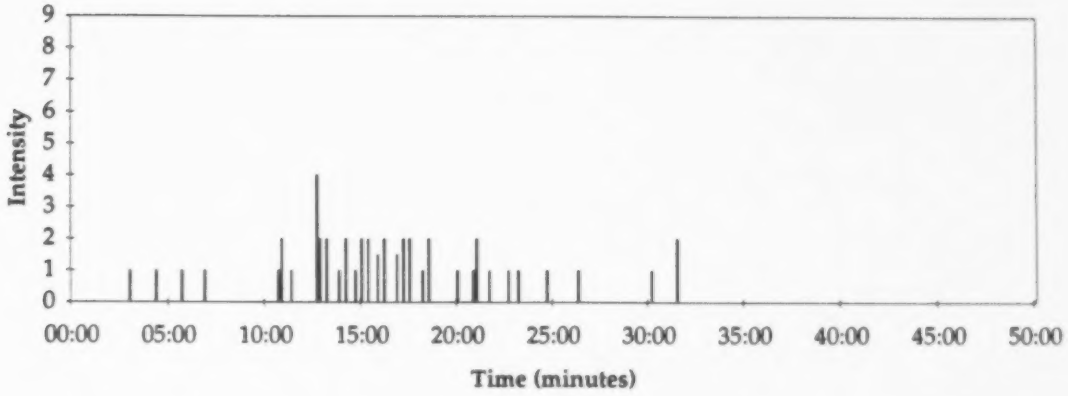
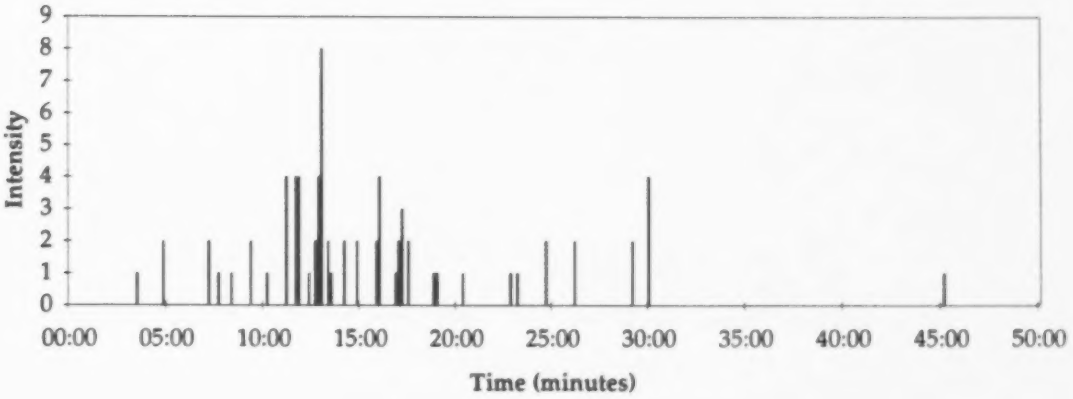


Figure 5.3 Odourgrams of the Dichloromethane Extracts from 4/5 April 1989

Raw



Treated without PAC



Treated with PAC

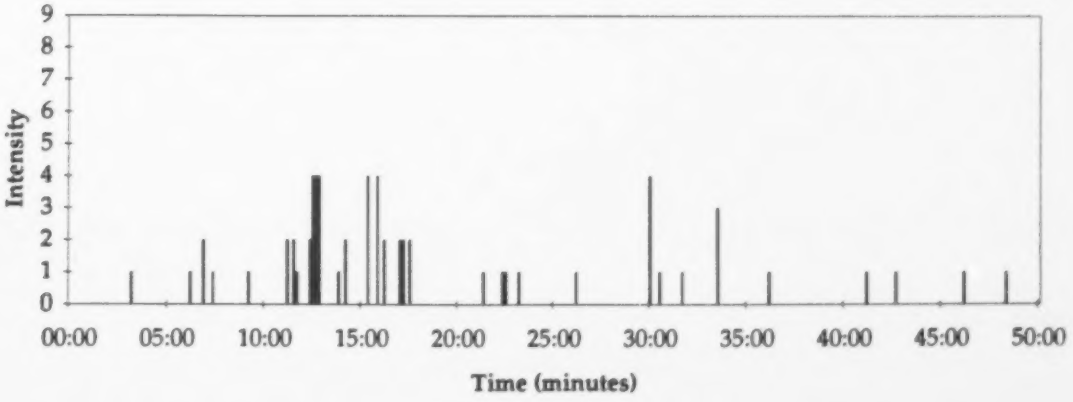


Figure 5.4 Geosmin in the SIM Scan of the Hexane Extract of 5/6 April 1989

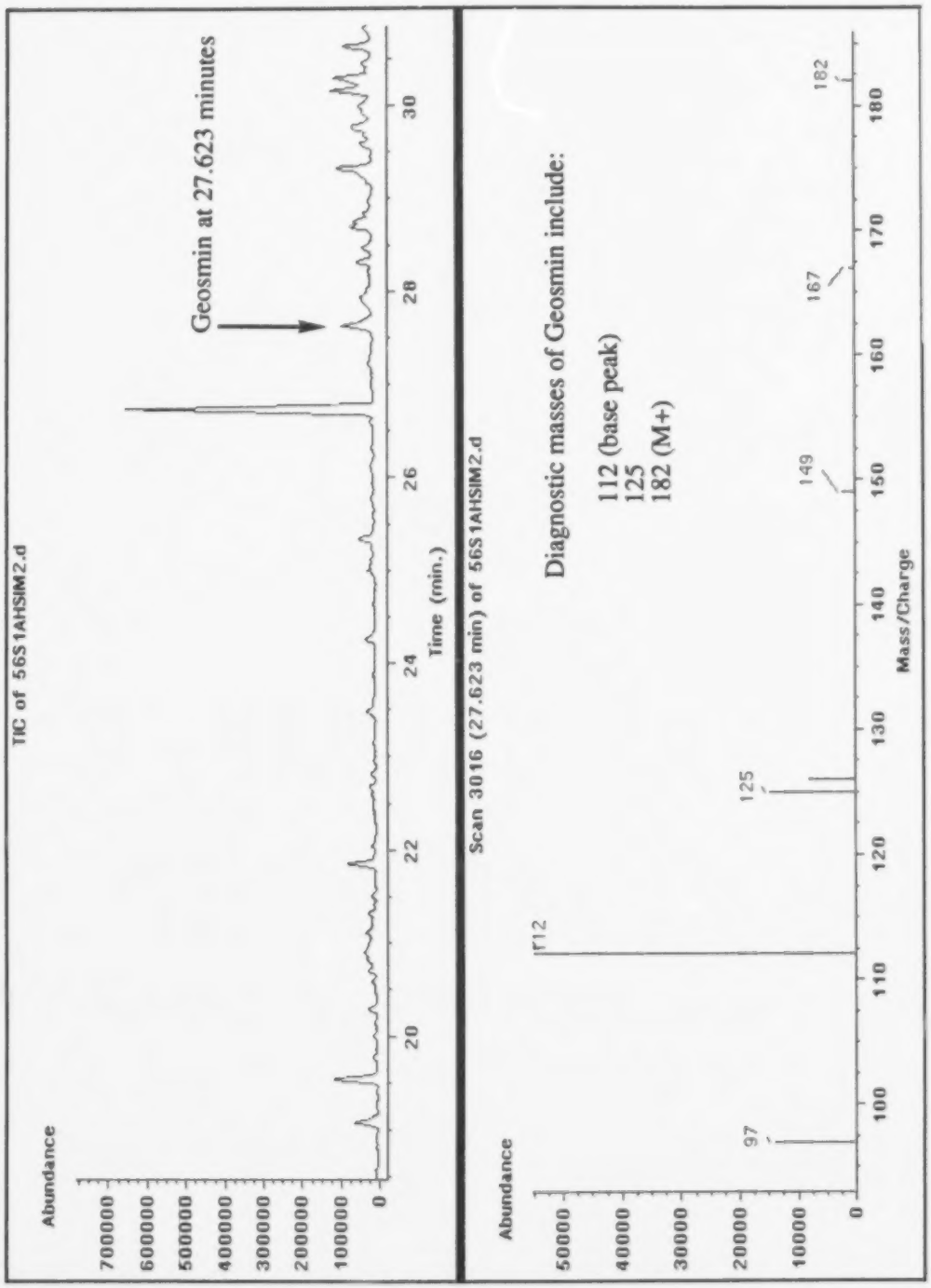


Figure 5.5 2-Methylisoborneol in the SIM Scan of the Hexane Extract of 5/6 April 1989

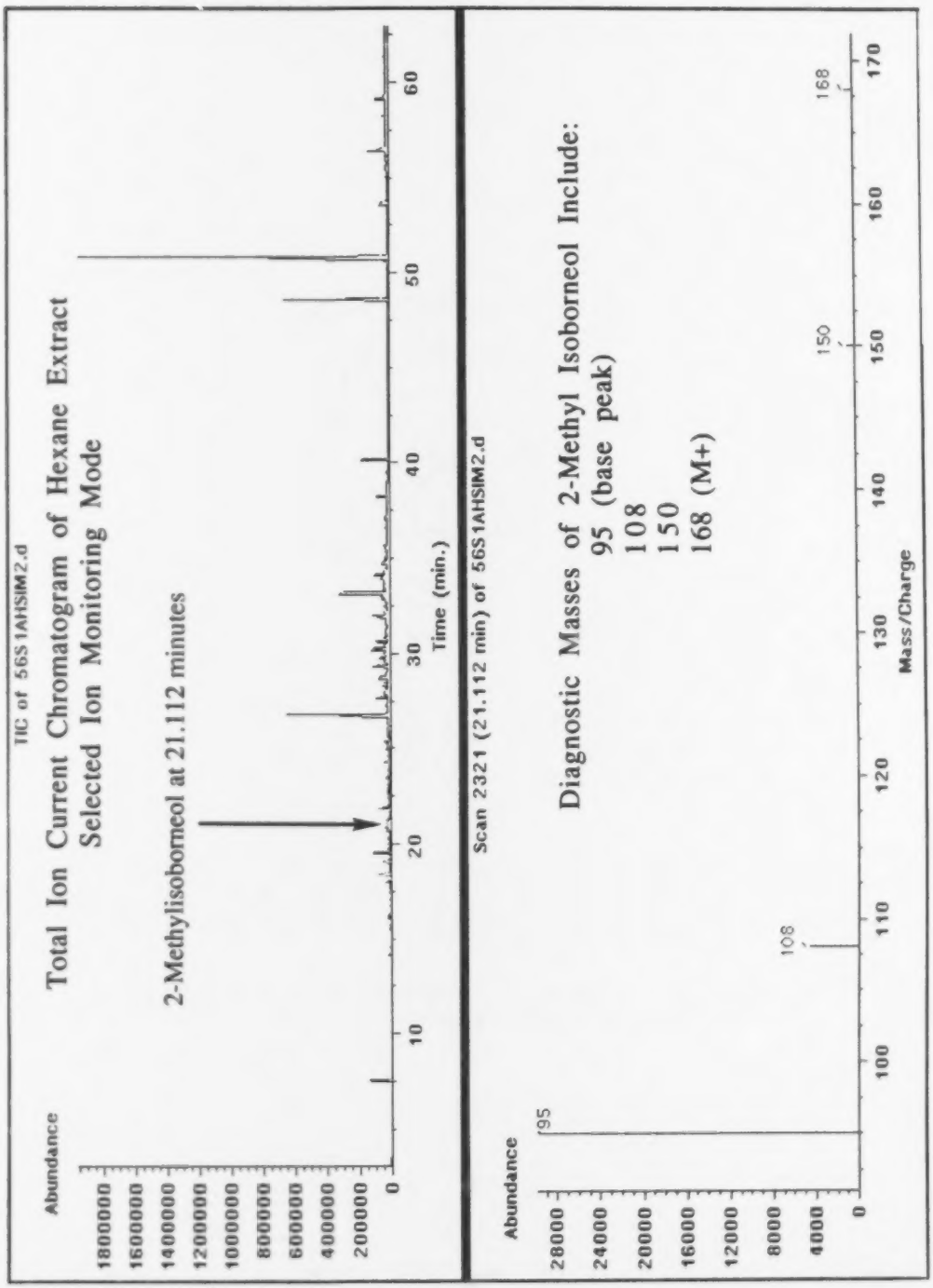


Figure 5.6 Geosmin in Full Scan and Extracted Ion Current Profile of Hexane Extract of 7/8 April 1989

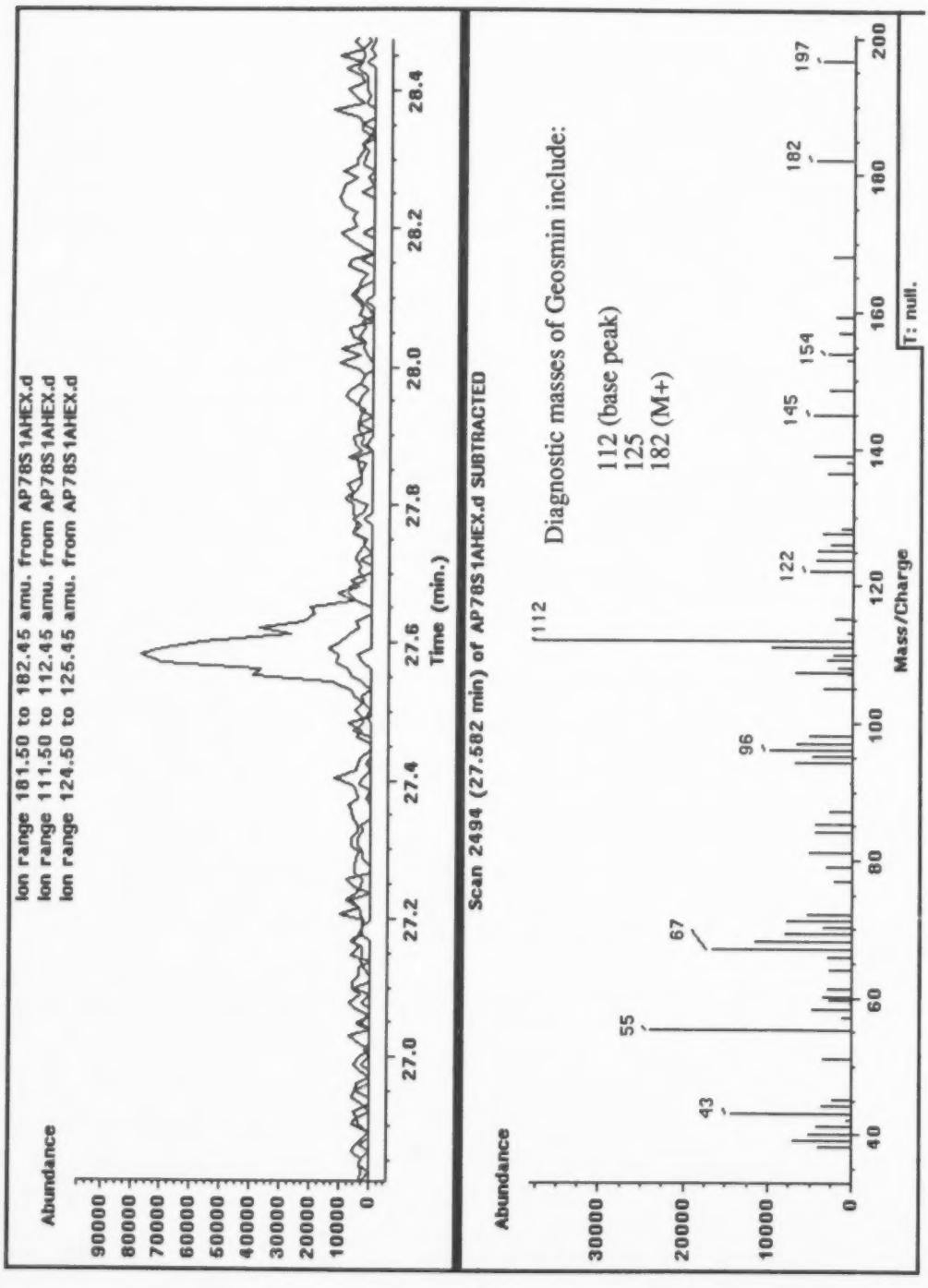


Figure 5.7 Mass Spectral Comparison of Standard and Sample Camphor

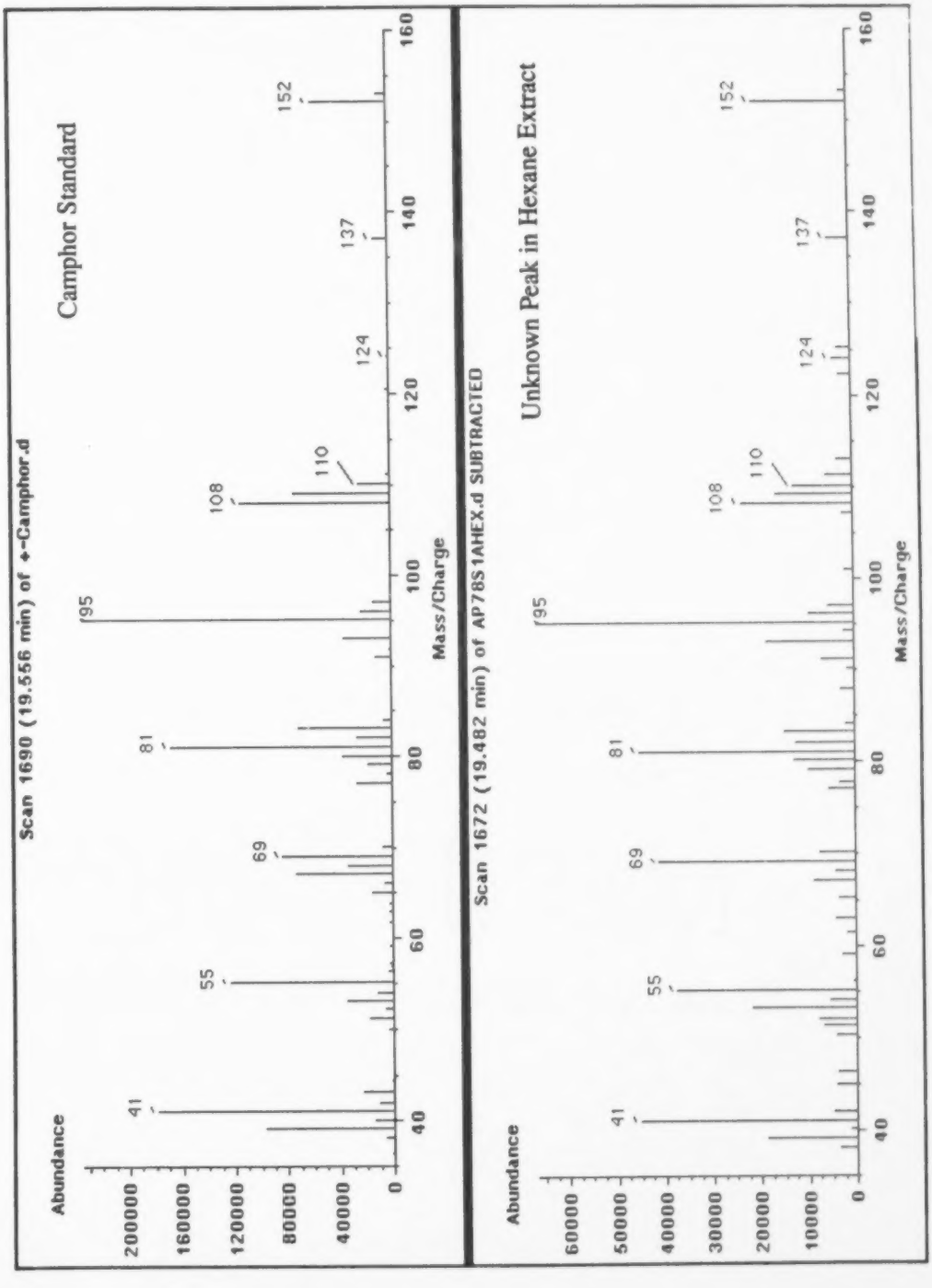


Figure 5.8 Mass Spectral Data for Molecular Sulfur

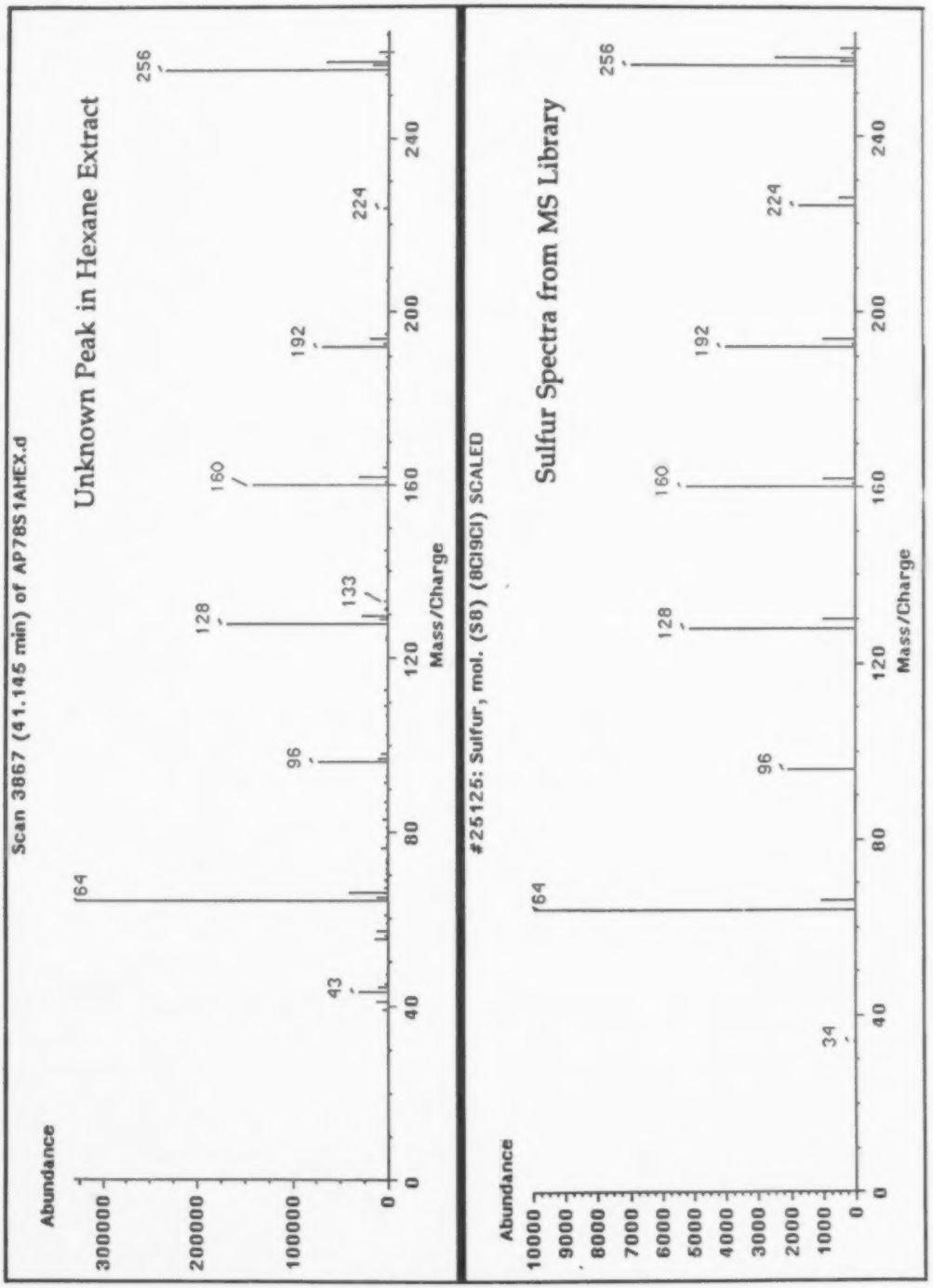


Figure 5.9 Mass Spectral Data for Dimethyl Disulfide

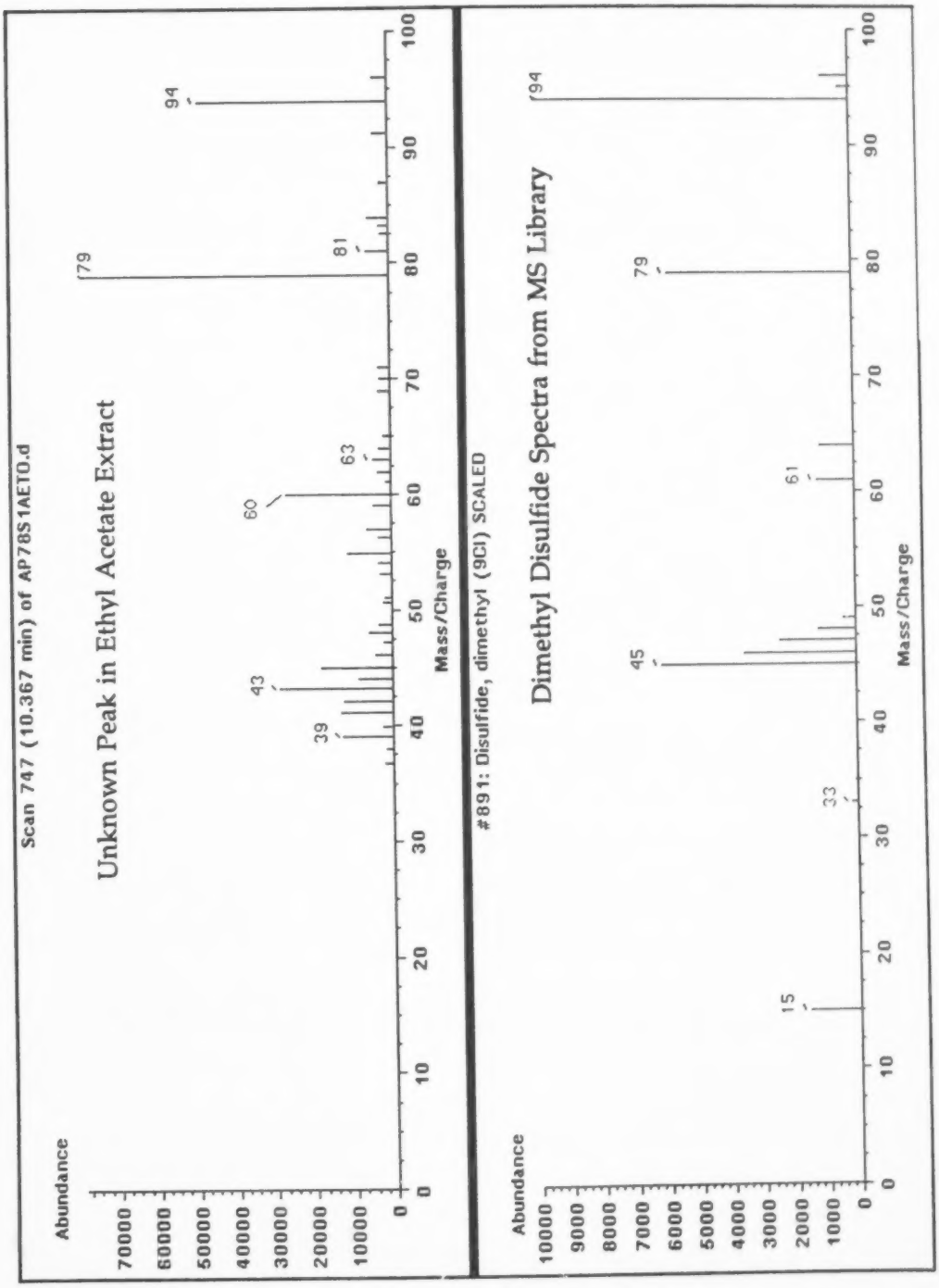


Figure 5.10 Mass Spectral Data for Sulfonyl bis Methane

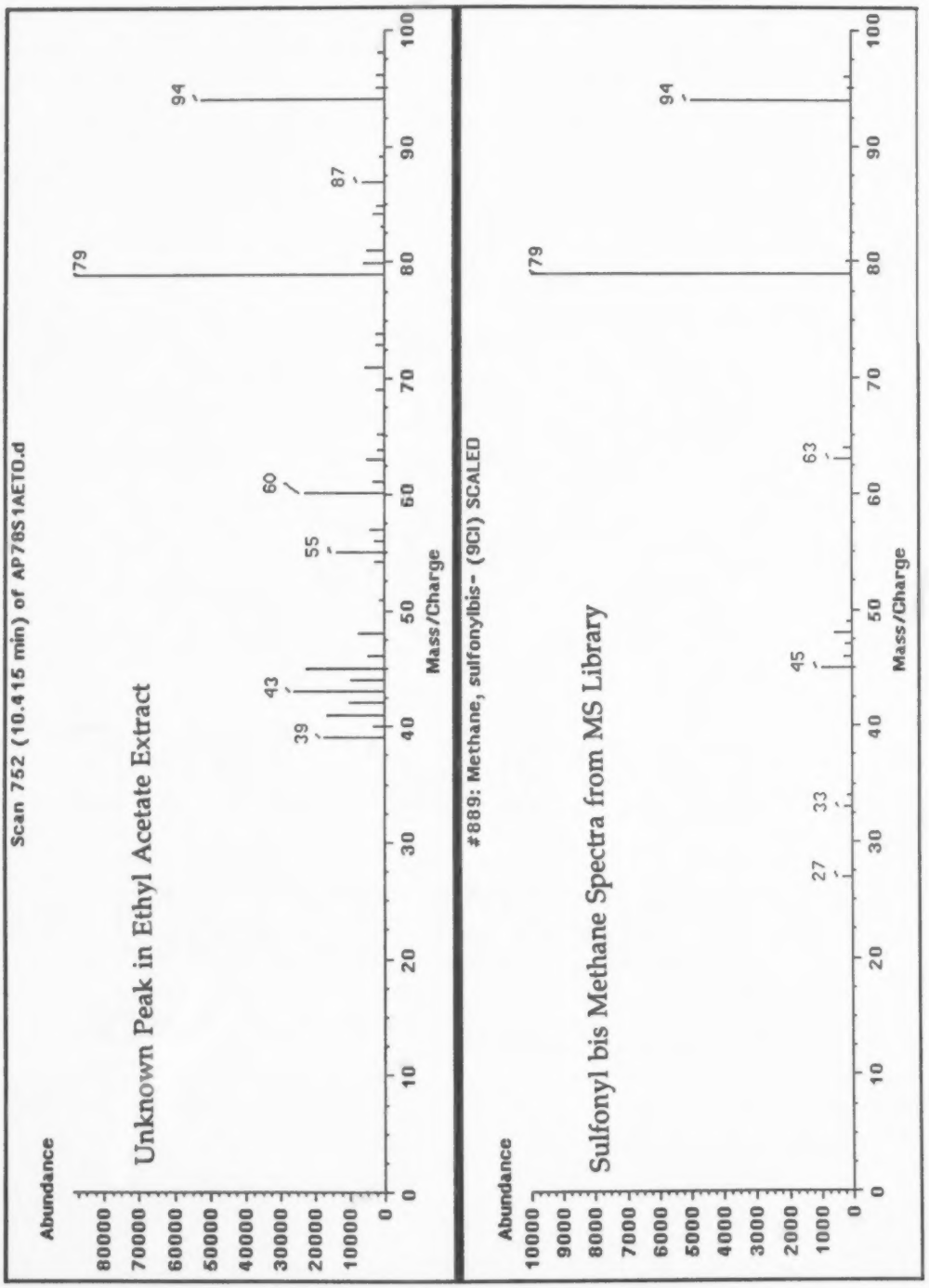


Figure 5.11 Mass Spectral Data for Hexanethiol

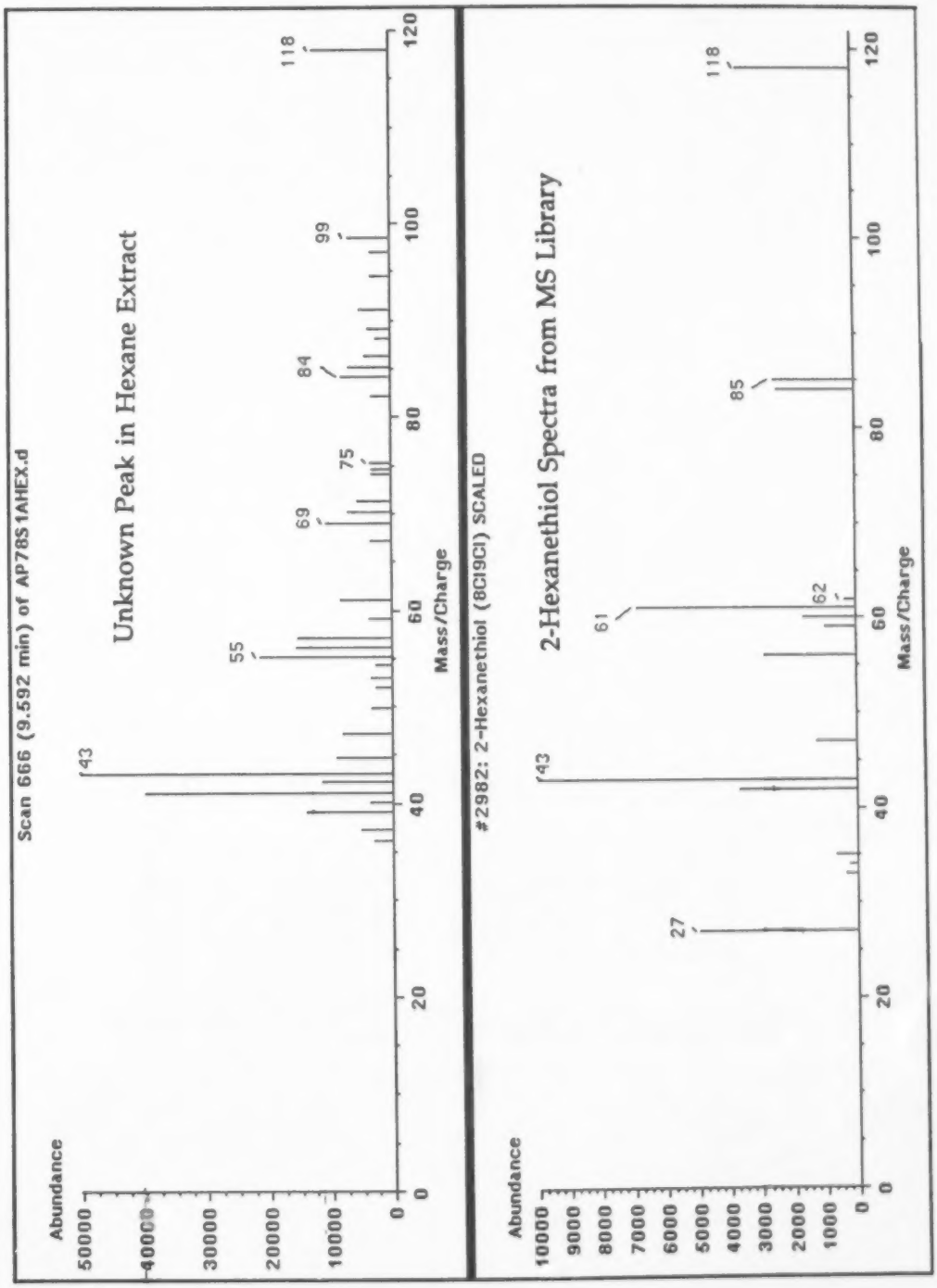


Figure 5.12 Mass Spectral Data for Dihydroactinidiolide with Library Match

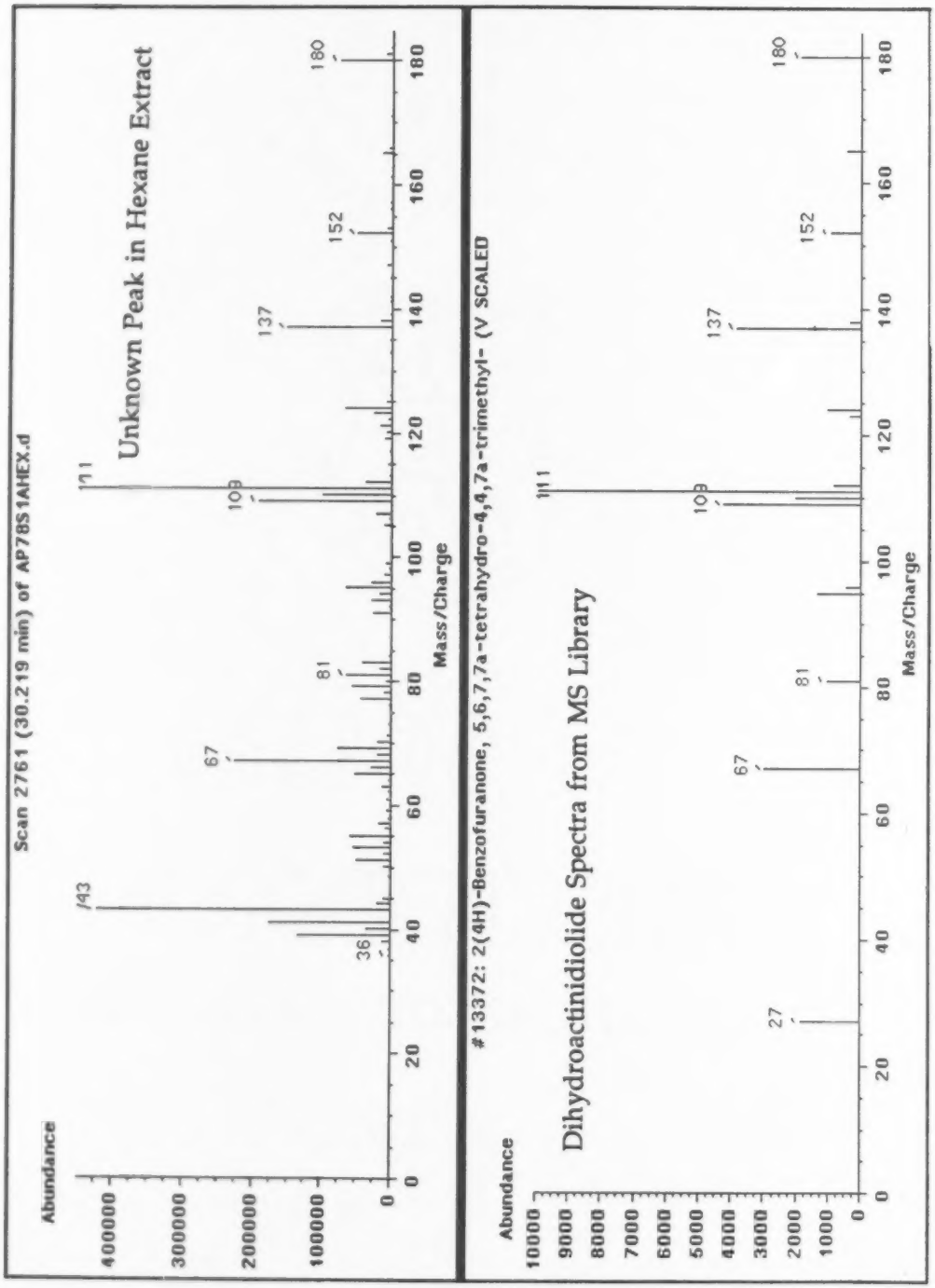


Figure 5.13 Mass Spectral Data for 3,7-Dimethyl-7-Octenal

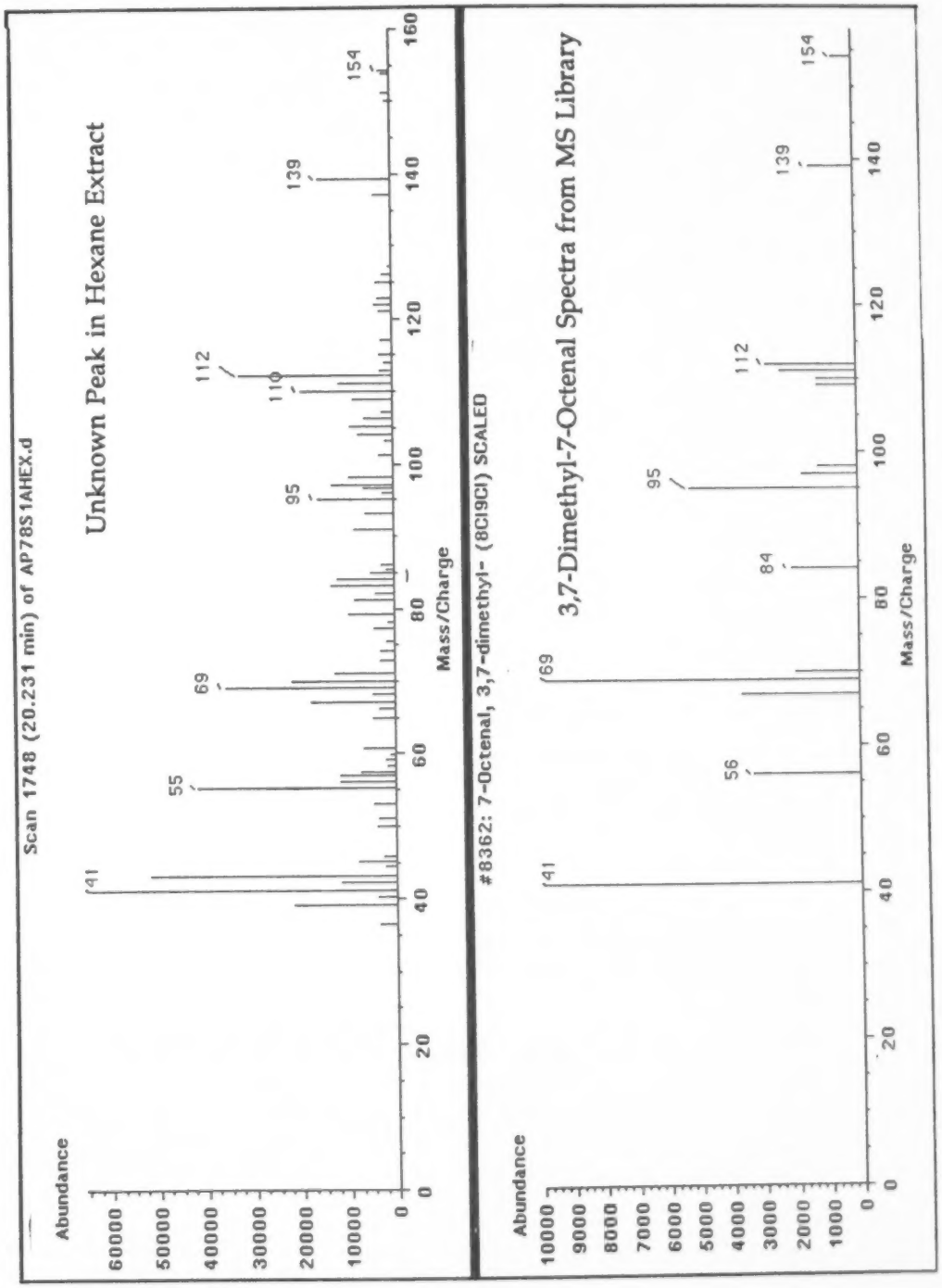


Figure 5.14 Mass Spectral Data for 2-Methyl-2-Pentenal

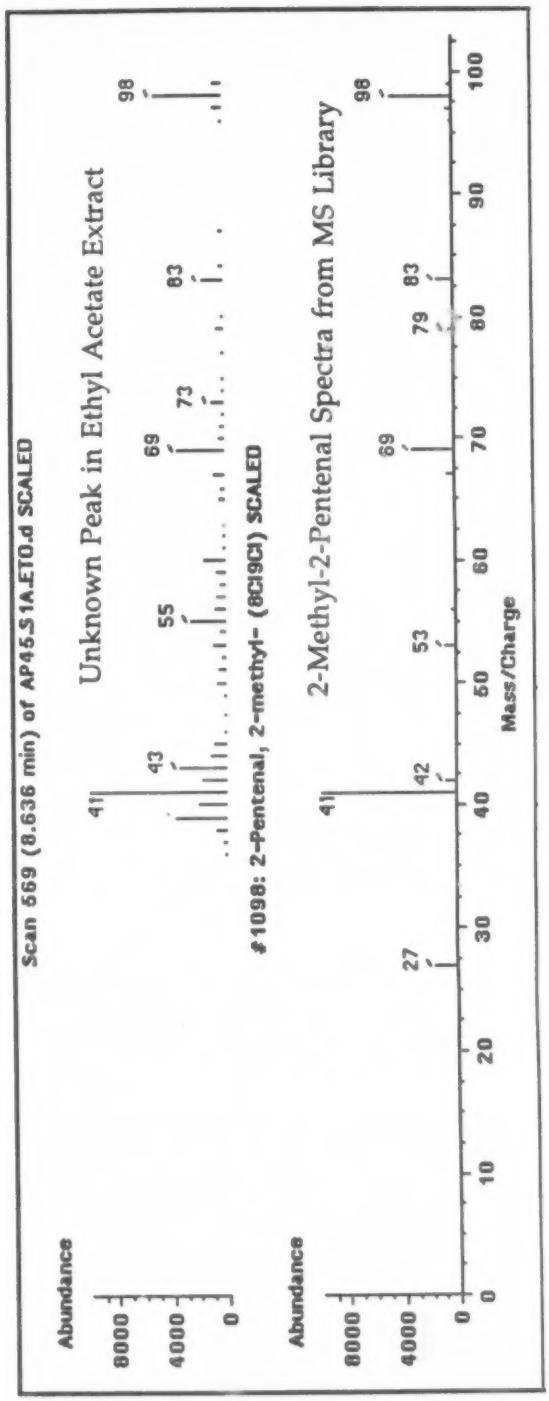

Scan 569 (8.636 min) of AP45_S1A_ETO.d SCALED
Unknown Peak in Ethyl Acetate Extract
#1098: 2-Pentenal, 2-methyl- (8CI9CI) SCALED
2-Methyl-2-Pentenal Spectra from MS Library
Abundance
Mass/Charge

Figure 5.15 Mass Spectral Data for Benzaldehyde

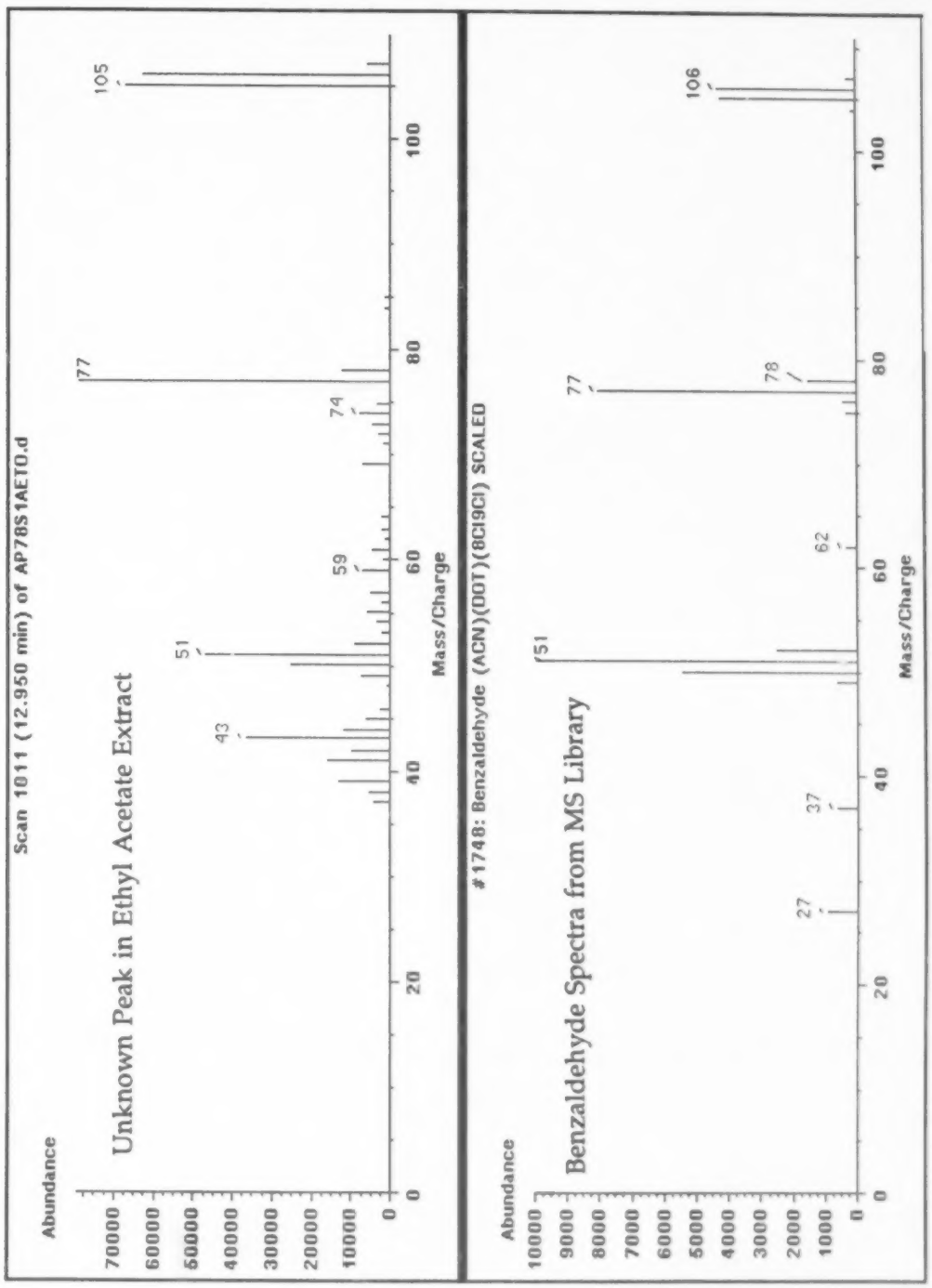
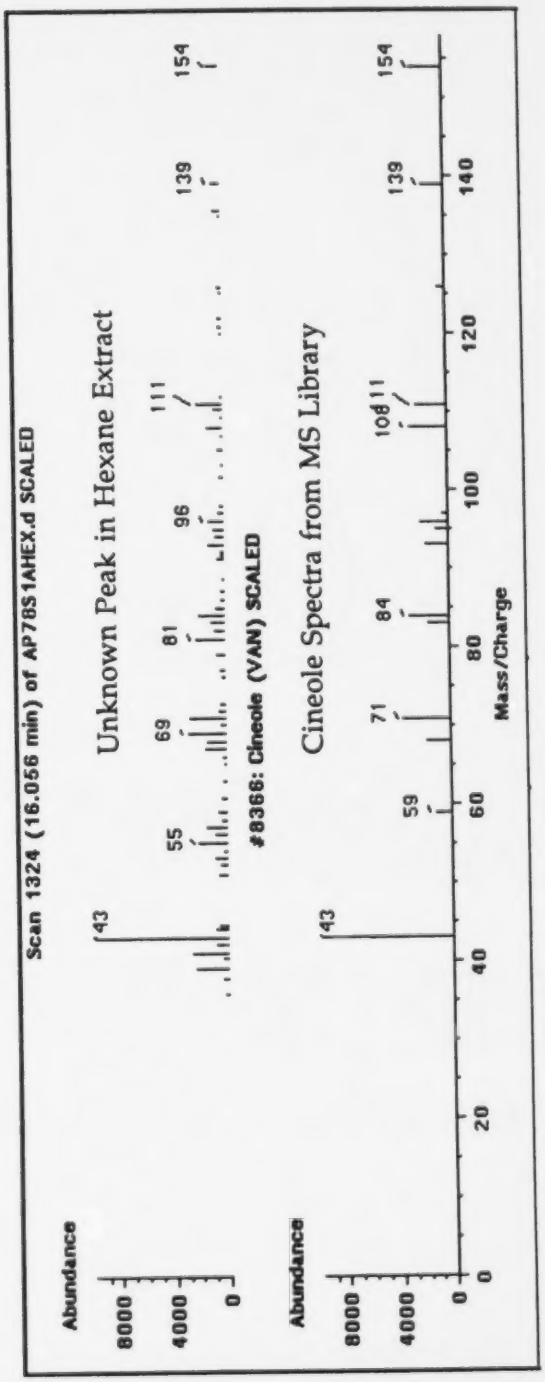


Figure 5.16 Mass Spectral Data for Cineole



6.0 Discussion

6.1 Solvent Extraction Efficiency

The granular activated carbon (GAC) used for this work was obtained by passing approximately 2000 L of raw or treated water through the column with the expectation that most of the relevant organics in the water would be adsorbed onto the surface of the carbon for subsequent extraction. Table 5.3 contains recovery data for selected organics that were spiked into organically pure water, adsorbed onto the GAC and then recovered by Soxhlet extraction. The results indicate that these odorous compounds can be reasonably quantitatively recovered after having been adsorbed by virgin carbon. The recoveries of these compounds, however, were significantly reduced when organically preloaded carbon was used. The latter is closer to the situation that had to be dealt with.

Chriswell et al. (1977) compared resins and activated carbon for the extraction of organics from water. They found that recoveries of model compounds depended upon solute, extracting solvent and the sorbent. In comparison, the results reported here are significantly better than those reported by Chriswell et al. (1977).

Lalezary-Craig et al. (1988) have shown in their work with GAC and powdered activated carbon (PAC) that adsorption of geosmin and 2-methylisoborneol was reduced in the presence of humic material, chlorine and/or monochloramine. They found that the adsorptive removals of 2-methylisoborneol were reduced by 82% in the presence of monochloramine at 2 mg/L. The GAC samples used in these experiments were exposed to either humic material (raw water) or monochloramine (treated water).

One of the objectives of this research was to develop an extraction process to remove the adsorbed organics from the GAC. Soxhlet extraction for 20 hours was expected to quantitatively remove any solute that was soluble in each of the various solvents. Loper et al. (1985) used a single solvent, dichloromethane, to Soxhlet extract (24 hours) the GAC. That treatment may not have removed all of the sorbed material. Five extractions were performed consecutively with different solvents in this research. The purpose of using the solvents of varying polarity was to desorb the solutes of varying polarity and is based on the principle of 'like dissolves like'. After 20 hours of extraction if a compound was likely to desorb at all, it would be

expected to do so quantitatively. As can be seen in the extracts of 5/6 April 1989 (Tables B.7, B.8 and B.9), geosmin, at the approximate RT 31.20, was present in all three solvents sniffed, namely hexane, ethyl acetate and dichloromethane. This indicated that the use of a single solvent to extract GAC to determine the concentration in the water would seriously underestimate the compound's concentration.

There are three possible explanations for this incremental desorption. First, the compounds themselves may be bound very tightly to the carbon and are only slowly removed, i.e. the desorption is kinetically controlled, more a function of extraction time, than the solvent properties. Thakker and Manes (1987) note that some compounds were irreversibly bound to the carbon and they had to employ displacers to dislodge the compounds of interest. The second possibility is that the solvent used initially was inefficient in removing these compounds and if an alternate solvent such as dichloromethane was used first, improved recoveries may have been realized. Chriswell et al. (1977) found there was no universal solvent to be used in extracting organics from activated carbon as each of the five solvent schemes used had better recoveries for some compounds and worse for others. In their experiments, they used pentane/acetone (4:1), diethyl ether, DCM/acetone (1:1), chloroform/acetone (1:1) and acetone to recover model compounds such as alkanes, esters, aromatics, phenols, amines, carboxylics and chlorinated compounds. The broad spectrum approach used in this research did not allow for the optimization of recoveries based on one specific compound as the source of the odour problem was not known in advance.

The third possibility relates to the miscibility of the solvents which was a concern as the GAC was fully saturated with water. From the moisture contents performed on the samples, it was found that the GAC sample placed in the Soxhlet apparatus generally contained approximately 60% water by weight. The solvent used first, hexane, is hydrophobic and any solute extracted would have to partition into the water phase prior to entering the organic phase. In order to overcome this, one could employ a two solvent system such as hexane/acetone or dichloromethane/acetone which would allow the solvent to have intimate contact with the solute laden carbon surface. Another option would have been to freeze-dry the carbon prior to extraction or dry it slowly in an oven (Buelow et al., 1973a) to reduce the moisture contents to the level of the virgin carbon (3%). Although the

adsorptive capacities of the carbon are not altered by freeze drying (Huck et al., 1988), the effect of this procedure on possible losses of the adsorbed organics is unclear. However, it seems likely that some of the volatile components may be lost and removed with the water vapour. As some solutes are tightly bound to the carbon surface, the freeze drying procedure may not remove significant amounts of the sorbed material while removing much of the interfering water.

During the spring runoff event, it was noted by those working on Alberta Environment's mobile water treatment plant, that some of the cartridges had became plugged due to the very high turbidities experienced during the spring runoff. The operational staff were focussing on reproducing the taste and odour events experienced in previous years through variation in disinfection practice and maintaining the process. Prior to plugging off completely, the flow through the column would have gradually reduced until no water could pass through it. Therefore, the actual quantity of water that passed through these cartridges (nominally 2000 litres), was unfortunately not known.

6.2 GC Sniffing

6.2.1 Safety of the Sniffing Procedure

Because of the wide range of the compounds contained in the extracts, and their potential toxicity, it was deemed prudent to review and determine the potential health consequences of the sniffing procedure. This procedure is widely used in the water treatment industry and the food industry (see section 2.2.2.3). Others have implemented this procedure in the analysis of surface water systems that are extremely polluted with industrial wastewaters and pulp mill effluents (Savenhed et al. 1985). However, no specific review of the hazards of this procedure was found.

Intuitively, the procedure does not seem to be hazardous due to the small volumes of sample extract (2 µL) used in the sniffing procedure. This conclusion was shown to be valid as odour peaks arising from the solvents were infrequently noted and when they were, they were of low intensity. Exposure levels to solvents are much higher during a liquid-liquid extraction with separatory funnels as the odours are very distinct and continuous over the period of the extraction. During these manipulations of the sample, the analyst is invariably exposed to fumes from the solvent.

As the carbon cartridges had a maximum of approximately 2000 litres of water passed through them, the 2 µL of extracted sample injected contained the organics present in 3.2 L of raw or treated water as shown below.

2000 L of water were passed over 200 g of virgin carbon
2000 L/200 g of carbon = 10 L/g carbon

40 g of original 200 g carbon Soxhlet extracted
40 g* 10 L/g = 400 L of water extracted into solvent

solvent sample reduced to approximately 250 µL and 2 µL injected
calculated water volume injected = (400 L /250 µL) * 2 µL = 3.2 L

This can then be compared to the average daily intake of tap water of 0.43 L for a child and 0.64 L for an adult (U.S. EPA 1984). This 3.2 litres concentration volume from the 2 µL injected, overestimates the exposure as it assumes the following:

1. that all of the compounds are absorbed during sniffing with no losses when exhaling or losses due to missed peaks when exhaling.
2. that all of the compounds in the extract are inhaled. Much of the 'peak' is rapidly carried past the nose on the column of warm air rising from the heated detector.
3. that 2000 litres were extracted when it is known that the flow rates decreased, and in some cases stopped, during the extraction due to plugging of the cartridges.
4. that all of the compounds were quantitatively adsorbed and subsequently quantitatively desorbed. The presence of geosmin and MIB in successive extractions with different solvents indicates that this quantitative desorption did not occur.

The largest component of the 2 µL sample is the solvent. This may prove to be the largest problem of this method when considering that one of the solvents, dichloromethane, is classified as a probable human carcinogen (ILO 1991). The time for each solvent to elute is well known and reproducible (186 seconds for hexane, 300 seconds for ethyl acetate and 84 seconds for

dichloromethane). From these times, a conservative exposure concentration can be calculated using the inhalation rates contained in Table 6.1. The inhalation rate for the sniffing procedure is between resting and light which corresponds to 0.7 and 0.8 m^3/hr for men and 0.3 and 0.5 m^3/hr for women. As one sniffer was female, the lowest rate for women was used for calculation purposes as it was the most conservative and provided the maximum concentration of the chemical.

Table 6.1 Human Inhalation Rates by Activity Level (m^3/hr)
(after Konz et al. 1989)

Subject	Resting	Light	Moderate	Heavy
Adult Male	0.7	0.8	2.5	4.8
Adult Female	0.3	0.5	1.6	2.9
Average Adult	0.5	0.6	2.1	3.9
Child Age 6	0.4	0.8	2.0	2.4
Child Age 10	0.4	1.0	3.2	4.2

The maximum (i.e. overestimated) exposure concentration was determined as follows:

Mass DCM = volume DCM x Density DCM (where DCM = dichloromethane)
= 2 µL x 1.33 mg/µL = 2.65 mg

Volume of air inhaled during exposure = inhalation rate x exposure time
= 0.3 m^3/hr x (hr / 3600 sec) x 84 sec = 0.007 m^3

Calculated exposure concentration = mass DCM / volume of air inhaled
= 2.65 mg / 0.007 m^3 = 379 mg/m^3

The calculated exposure concentration to DCM (379 m^3/hr) was slightly higher than the TLV-TWA of 360 mg/m^3 but was less than one quarter of the short term exposure level (TLV-STEL) of 1700 mg/m^3 (Table 6.2). The TLV-STEL values are based on exposures with durations of no more than fifteen minutes with a minimum of sixty minutes between exposures (ACGIH 1984). As noted above, the exposures to the solvents ranged from 84 seconds to 300 seconds, which are well below the fifteen minute exposure maximum. As

Table 6.2 Threshold Limit Values - Time Weighted Averages (TLV-TWA)

Chemical	TWA (mg/m3)	STEL (mg/m3)	Source
Solvents			
Acetone	1780	2375	1
Benzene	30	75	1
Butanol	150		1
Carbon tetrachloride	30	125	1
Cyclohexane	1050	1300	1
Cyclohexanol	20		1
Cyclohexanone	100	400	1
Cyclohexene	1050	1300	1
Ethanol	1900		1
Ethyl acetate	1400		1
Ethyl benzene	435	545	1
Heptane	1600	2000	1
n-Hexane	180		1
Hexane isomers (not n)	1800	3600	1
n-Hexanol	10		2 (USSR)
Isobutyl alcohol	150	225	1
Isopropyl alcohol	980	1225	1
Methyl alcohol	260	310	1
Methylene chloride	360	1700	1
Xylene (all iso)	435	655	1
Methyl propyl ketone	700	875	1
Toluene	375	560	1
Octane	1450	1800	1
Pentane	1800	2250	1
Perchloroethylene	340	1340	1
Other Chemicals			
Acetaldehyde	180	270	1
Acetic Acid	25	37	1
Benzaldehyde	80		2 (Japan)
Bromoform	5		1
Butyl mercaptan	1.5		1
Camphor	12	18	1
Chlorobenzene	350		1

Table 6.2 (cont'd) Threshold Limit Values - Time Weighted Averages

Chemical	TWA (mg/m3)	STEL (mg/m3)	Source
Chloroform	50		1
Chlorotoluene	250	375	1
Cumene	245	365	1
o-Dichlorobenzene		300	1
p-Dichlorobenzene	450	675	1
Ethyl mercaptan	1	3	1
Formaldehyde	1.5	3	1
Gasoline	900	1500	1
2-Hexanone	100	165	2
Hydrogen sulfide	14	21	1
Methyl cyclohexane	1600	2000	1
Methyl cyclohexanol	235	350	1
Methyl mercaptan	1		1
Phenol	19	38	1
Resorcinol	45	90	1
Naphthalene	50	75	1
Trimethyl benzene	125	170	1
n-Valeraldehyde	175		1

Sources:

1. Documentation of the Threshold Limit Values Fourth Edition, American Conference of Governmental Industrial Hygienists Inc. 1984.
2. Occupational Exposure Limits for Airborne Toxic Substances, Second Edition, International Labour Organization,1980

each sniffing run required 2 to 2.5 hours to complete, the minimum time between solvent exposures was also met.

As an additional check, the mass of solvent that can be inhaled during the TLV-STEL of 15 minutes can be determined and compared to the volume of sample injected for DCM.

Permissible Mass Inhaled = Air Inhaled in 15 minutes x TLV-STEL
= (0.3 m^3/hr) / 4 x 1700 mg/m^3
= 127.5 mg

Permissible Volume Inhaled = Mass Potentially Inhaled / Density of DCM
= 127.5 mg / 1.33 mg/µL
= 95.9 µL of DCM

As shown above, the maximum permissible volume of DCM that one can inhale during a 15 minute exposure is almost 50 times greater than the total volume of solvent injected onto the head of the column (i.e. 2 µL).

Similar calculations were completed for the other two solvents. For hexane, the calculated exposure concentration was determined to be 85 mg/m^3. This compares favourably to a TLV-TWA of 180 mg/m^3. The TLV-TWA for ethyl acetate was 1400 mg/m^3 and the calculated exposure concentration was determined to be significantly less at 72 mg/m^3. From these calculations, it was determined that the sniffing procedure, in relation to the solvent peaks, was consistent with acceptable occupational exposure levels.

The determination of the hazards associated with the other constituents in the solvent extracts is more problematic as the concentrations of many of the components are unknown and many of the components were unidentified. In reviewing the total areas of the chromatograms, it was noted that the solvent peaks had by far the largest areas. For hexane, the area associated with the solvent peak was 98.9% of the total area with no single non-solvent peak greater than 0.089% of the total area. The remaining 1.1% of the total area was derived from 159 distinct peaks. Assuming that all of the peaks were the same size, and that all of the components gave the same response to the FID, it can be shown the mass of the separate compounds was at least 10,000 times less than the mass of the solvent injected (i.e.

1/(1.1%/98.9%/159 peaks) = 14,296). The total non-solvent area associated with the dichloromethane extracts was 0.32% with 45 peaks and for the ethyl acetate 6.94 % with 126 peaks. The larger area in the ethyl acetate extracts was due to artifacts generated by the solvent as noted by the mass spectral data which contained numerous carboxylic acids and acid esters. The peaks from these compounds were very broad which is characteristic of carboxylic acids using the DB-1 column with flame ionization detection. These compounds have TLV-TWA's in the range of 835 mg/m^3 for propyl acetate and 950 mg/m^3 for the butyl acetate isomers.

As a first approximation, the concentrations of the unknown compounds were determined by using the response factor from a known compound which gave a poor response using GC-FID. Using a compound providing a poor response provides maximum (i.e. conservative) exposures. This concentration was then used to determine an exposure factor which was compared to the TLV's. From the chromatograms it was determined that the response factors for the various solvents were 5.2×10^8 area counts/mg injected for hexane, 5.5×10^8 area counts/mg injected for ethyl acetate and 1.3×10^8 area counts/mg injected for dichloromethane. These values were relatively close considering the various functionalities of the solvents which range from an aliphatic hydrocarbon to an ester to a polychlorinated compound. As the dichloromethane had the lowest response factor, it was used for calculations as it would tend to overestimate the concentration of organic compounds. The largest total non-solvent area in any of the chromatograms had area counts of 74395889 (6.94% of the total area) in the ethyl acetate extract. As previously noted, the large peaks in the ethyl acetate chromatogram were due to solvent artifacts and were identified. Although the exposure due to the organics producing this area occurred over 50 minutes, the exposure time was assumed to be 15 minutes as this was the time used to generate STEL's and would therefore overestimate acute exposures.

Calculated mass of unknown = Area counts of largest peak / FID response factor for DCM

= 74395889 area counts / 1.3×10^8 area counts per mg = 0.57 mg

Volume of air inhaled during exposure = inhalation rate x exposure time

$= (0.3\ m^3/hr) \times (hr / 3600\ sec) \times 900\ sec = 0.075\ m^3$

Calculated exposure concentration = mass unknown / volume of air inhaled
$= 0.57\ mg / 0.075\ m^3 = 7.6\ mg/m^3$

This value ($7.6\ mg/m^3$) is much below the TLV values for the acetic acid derivatives which have TLV's between 800 and 1000 mg/m^3 (ILO 1991).

All of the other peaks in the chromatograms not associated with the solvent were below one million area counts. Similar calculations (using one million area counts) to the above provides an exposure concentration of 0.10 mg/m^3 which compares favourable to most of the TLV's from the ACGIH (1980). However, TLV's for mixtures must be calculated by dividing each concentration by the specific TLV and summing them. Should the summed value be greater than one, the threshold limit should be considered exceeded. Therefore, the total non-solvent area was used to calculate a total mass to determine the total concentration. The total non-solvent area in the hexane extracts was found to be 7685548 area counts which corresponds to a mass of 0.059 mg when the response factor for dichloromethane was used. The total air inhaled in one hour was 0.3 m^3 giving an exposure concentration of 0.20 mg/m^3 over one hour or 0.025 mg/m^3 per day. The ACGIH (1980) notes that the TLV's are guides and that the time weighted averages permit excursions above the limit provided they are compensated for by equivalent excursions below the limit during the day. The lowest TLV-TWA noted by the ACGIH (1980) was 0.001 ppm (0.0033 mg/m^3) for bis- (chloromethyl) ether, a known carcinogen. These calculations were based on the total of the non-solvent peaks and it would be unlikely that the TLV-TWAs would be the same. Most TLV-TWAs were many orders of magnitude higher as indicated in Table 6.2. ACGIH also notes that the amount that the TLV can be exceeded is a function of the nature of the contaminant, cumulative effects, frequency of high exposures and the duration of such periods.

As noted earlier, it is instructive to work backwards from the TLV-TWA and determine the exposure one could expect in an industrial setting. As the TLV-TWA's are conservative it would be reasonable to assume the following:

- 8 hour exposure

- adult male (highest respiration rate)
- heavy activity level (highest respiration rate)

Therefore, the total permissible exposure can be calculated for the lowest TLV-TWA noted (i.e. bis(chloromethyl)ether).

Permissible Mass Inhaled = Air Inhaled in 8 hours x TLV-TWA
= (4.8 m^3/hr) x 8 hours x 0.0033 mg/m^3
= 0.127 mg

Permissible Volume Inhaled = Mass Potentially Inhaled / Density of Ether
= 0.127 mg / 1.315 mg/µL
= 0.096 µL of bis(chloromethyl)ether

To reach the level of exposure permissible according to the TLV-TWA, almost 5% of the total volume injected would have to be bis(chloromethyl) ether (i.e. 0.096 µL / 2 µL x 100). As discussed earlier, the total non-solvent peak areas were 1.1% for hexane, 0.32% for dichloromethane and 6.94% for ethyl acetate. The larger area for ethyl acetate was composed of 126 distinct peaks, the largest of which were identified as carboxylic acids and esters derived from the ethyl acetate.

Consequently, even under the worst case of bis(chloromethyl)ether, it was determined that there were no safety problems associated with the sniffing procedure. During the experiments, there were no adverse physical effects noted such as headaches, drowsiness or tissue damage that one would expect if the levels of some toxic compounds were high.

6.2.2 Sniffing Blanks

In reviewing the blanks contained in Tables B.1, B.2 and B.3, one can see that some of the odours detected in the samples were also from the blanks. Some of these odours were very intense as was the case of the vitamin C odour at RT 12.45 and the hydrocarbon/skunky odour at RT 15.44. The hexane blanks had only one significant odour (vitamin C) in the virgin carbon blank and none in the solvent blank.

The dichloromethane blanks gave similar results as there were no significant odours in the solvent blank and three in the virgin carbon blank.

This blank contains the two odours mentioned above as well as a weak skunky odour at RT 10.38. The dichloromethane extracts of 4/5 April 1989 had a skunky odour at RT 10.38, 11.06, and 11.12 for the raw, treated with PAC and treated without PAC respectively. Some of the hexane extracts (i.e. 4/5 and 6/7 April 1989) also had a skunky odour at RT 10.33 but the blank hexane did not. The mass spectral analysis of a hexane extract had a fair correlation for hexanethiol at the converted (to sniff time) retention time of 10.50. This compound has an OTC of 11.8 µg/L in air (van Gemert and Nettenbreijer 1977). As the odour was not in the hexane or ethyl acetate blank, was not in all of the samples and was only a weak odour in the blank, it could not be concluded that the skunky odour in the samples was due to an artifact.

The vitamin C odour was at the correct retention time (approximately 12.45) in many of the extracts. In some of the samples the vitamin C odour preceded a hydrocarbon odour and in some, the hydrocarbon was at RT 12.45. Any peaks in this portion of the chromatograms with these types of odours were deemed to be from the blank GAC. Similarly, the hydrocarbon/ skunky odour at RT 15.44 was in many of the samples with the hydrocarbon and skunky being two distinct smells in some. There was a peak in the mass spectral data with an extremely good correlation which was found to be a trimethyl benzene at the corresponding retention time for the offending odour. The isomer with the lowest OTC was 1,3,5 trimethyl benzene and it has an OTC in water of 3 µg/L (van Gemert and Nettenbreijer 1977) and gives an earthy odour in water (Mallevialle and Suffet 1987).

The ethyl acetate blanks were much more complex with odour descriptors such as aldehyde or sweet in addition to the vitamin C odour. These are the types of odours that esters and aldehydes have and which can be expected when ethyl acetate is subjected to a harsh environment as was done in the Soxhlet extraction and Kuderna-Danish evaporation. The solvent was essentially refluxed for many hours with the highly reactive surface of the GAC. The formation of odorous esters and aldehydes was quite possible. Several authors have noted that the GAC can cause the formation of byproducts that were not due to the solute and solvent (Lalezary-Craig 1988, Jackson et al. 1987). There were some odours in the solvent blank, such as the strong aldehyde/sweatsocks at RT 11.35, that were not in the carbon extract blank when one would expect them to be present. The ethyl acetate sample extracts contained foul, sour or skunky smells at this retention time. One

possible explanation for this was that the odorous compound from the solvent may have a high affinity for the GAC surface and be preferentially adsorbed. This was even more reasonable when one considers that the GAC used for the blanks was virgin GAC with a large surface area and numerous adsorption sites available to take up the odorous artifacts.

As the GAC could not be fully drained of all the solvent between solvent changes there was the possibility of carry over from one sample to the next. The aldehyde odour in the 4/5 April 1989 dichloromethane extracts at RT 11.30 may be just such an example. This odour was not present in any of the dichloromethane blanks but it is in the ethyl acetate solvent blank as well as the ethyl acetate extracts from the same day. This peak was therefore assumed to be an artifact arising from the ethyl acetate.

6.2.3 Reproducibility of Sniffing

Two sniffing runs were completed by different sniffers in order to determine the interperson variations with respect to retention time, odour detection/strength and odour description. The results of these runs on the hexane extract of the treated stream without PAC on 5/6 April 1989, are contained in Table B.11.

Sniffer #1 noted almost twice as many distinct odours as sniffer #2 (74 vs 39) with 29 of the odours being common to both odourgrams. This was not unexpected as sniffer #1 had significantly more experience with this technique and it was found that a number of runs were required to familiarize sniffer #2 to the various background odours of the column and heated detector. The errors involved with this method would tend to be ones of omission rather than commission as odours may be missed due to low intensity or breathing rates. Of the odours detected that were not in common, 32 detected by sniffer #1 were medium to strong whereas sniffer #2 had only 3 medium intensity odours not detected by sniffer #1.

The strength distribution of the odours for the two sniffers showed marked differences as indicated in Table 6.3. The different distributions may be accounted for by the inexperience of sniffer #2 who may not have had an accurate 'scale' from which to work as well as a relatively reduced sensitivity. This would cause some of the stronger odours detected by sniffer #1 to be given lower ratings by sniffer #2, and the weaker odours not being detected by sniffer #2 at all.

Both sniffers noted a number of odours with interesting descriptors that may be of importance in determining the cause(s) of Edmonton's taste and odour problem. Table 6.4 (extracted from Table 5.10), shows that the perceived odours can be described consistently between sniffers. Geosmin, the compound eluting at RT 31.04/31.09 minutes, is often described as producing an earthy/musty smell (Persson 1979) which was how the sniffers described it. Similar correspondence was shown for the other odours such as skunky, sewer and black cat gum.

Overall the reproducibility of the method between sniffers was quite good as can be noted by the small differences between retention times and the number of odours with the same or similar descriptors.

Table 6.3 Odour Distribution Between Sniffers

Odour Intensity	Sniffer #1 # Odours (%)	Sniffer #2 # Odours (%)
strong	19 (26%)	3 (8%)
medium	33 (45%)	12 (31%)
weak	22 (30%)	24 (62%)
total odours	74	39

Table 6.4 Reproducibility Between Sniffers*

Time (Sniffer #1/ Sniffer #2)	Sniffer #1 (D. Rector)	Sniffer #2 (N. Best)
1.48/1.48	sewer (w)	sewage (m)
5.25/5.22	hydrocarbon (s)	oil (w)
8.14/8.09	heavy hydrocarbon (s)	gas (s)
10.12/10.14	skunky (m)	skunk (m)
18.13/----	socks (s)	-
20.47/20.46	garden (s)	plants/grass (m)
25.17/25.19	camphor/menthol (s)	camphor (s)
28.23/28.24	black cat gum (w)	black cat gum (m)
30.31/30.31	old (m)	soil/greenhouse (m)
31.04/31.09	earthy (s)	musty mouldy (s)
40.37/40.52	spicy (m)	spicy (w)

* Treated water with no PAC addition from 5/6 April 1989
All Sniffing experiments conducted by D. Rector unless otherwise noted.

6.3 Compounds Identified in Extracts

A number of the extracts that possessed distinctive odours in the odourgrams were analyzed by gas chromatography mass selective detector. The tentatively identified compounds are listed in Table 6.5.

6.3.1 Geosmin and 2-Methylisoborneol

In most of the samples that were sniffed there were two odours at RT 24.33 and RT 31.20 minutes that had descriptors of camphor/menthol and lingering musty respectively. These odours and retention times closely matched those of the known taste and odour causing compounds 2-methylisoborneol and geosmin. Both of these compounds have very low odour threshold concentrations in water that are measured in the low ng/L range. At high concentrations 2-methylisoborneol is reported to have a camphor/menthol odour while at low concentrations it is perceived as a musty odour (Persson 1980b). Historically, musty has been one type of odour that has caused problems in Edmonton's drinking water (Hrudey 1986). These samples were then subjected to gas chromatography-flame ionization detection (GC-FID) and gas chromatography-mass selective detection (GC-MSD) in the electron ionization mode (EI), but the results did not indicate the presence of one or both of these compounds. The chromatograms, at the retention times that these compounds could be expected, were very complex and the odorous compounds would have to be in high concentrations to be detected.

Prior to the widespread application of mass spectrometry, confirmation of the presence or absence of a particular compound was accomplished by using different GC columns and noting if the retention time of the unknown peak still coincided with the new retention time of the standard on the new column. This method has also been used in the sensory analysis (GC-sniffing) of extracts to identify geosmin (Safferman et al. 1967) and microbially produced sulfur compounds (Jenkins et al. 1967). This method was employed to determine if indeed geosmin and/or 2-methylisoborneol were present.

Table 6.5 Tentatively Identified Compounds in Extracts

Benzene, Phenol & Derivatives
- 2-ethyl phenol
- 2-ethyl-phenol
- 2-methyl-phenol (or iso)
- 3-ethyl phenol
- 3-methyl phenol
- 3-propyl phenol
- 4-methyl phenol
- phenol
- 1-ethyl-2,3-dimethyl benzene
- 1-ethyl-2-methylbenzene
- 1-ethyl-3,5-dimethyl benzene
- 1-ethyl-3-methyl benzene
- benzene
- dimethyl benzene (all iso)
- ethyl benzene
- methyl benzene
- methyl(1-methylethyl) benzene
- propyl benzene
- trimethyl benzene (all iso)

Terpenoids, Furans & Derivatives
- 2-methyl isoborneol
- 3,6,6-trimethyl bicyclo[3.1.1]hept-2-ene (like a-pinene)
- 4,4,7a-trimethyl-hexahydro-2(3H)-benzofuranone
- 5,6,7,7a-tetrahydro-4,4,7a-trimethyl-2(4H)-benzofuranone
- 5-ethenyltetrahydro-5-trimethyl-2-furanmethanol
- 7,7-dimethyl-2-methylene-bicyclo[2.2.1]heptane (like ß-pinene)
- camphor (1,7,7-trimethyl bicyclo[2.2.1] heptan-2-one)
- cineole (1,3,3-trimethyl-2-oxabicyclo[2.2.2]-octane, eucalyptol)
- geosmin (1,10-trans-dimethyl-trans-(9)-decalol)
- tetrahydro-2,5-dimethyl furan

Cyclic Alkanes and Derivatives
- 1-methylcyclopentanol
- 2-methyl-1-cyclopenten-3-ol
- 2-methylpropyl cyclohexane
- 3-methyl cyclopentanol
- 3-methyl cyclopentanone
- 4-trimethyl-3-cyclohexene-1-methanol (terpineol)
- 2-cyclohexen-1-one
- cyclohexane
- cyclohexanol
- cyclohexanone
- cyclohexene
- propyl cyclohexane

Alkanes
- 1,3-hexadien-5-yne
- 1,5-hexadien-3-yne
- 2,3,6-trimethyl octane
- 2-methyl hexane
- 2-methyl nonadecane
- 3-methyl hexane
- 3-methyl nonane
- 3-methyl octane
- 4-methyl decane
- C6-C12, C19 alkanes
- 2-methyl-1-pentene

Aldehydes, Ketones & Alcohols
- 2-ethyl-2-hexanal
- 2-ethyl-2-hexenal
- 2-hydroxy benzaldehyde (salicylaldehyde)
- 2-methyl-2-pentenal
- 3,7-dimethyl-7-octenal (a-citronella)
- benzaldehyde
- phenanthrenecarboxaldehyde
- 2-hexanone
- 3-hexanone
- 3-methyl-2-pentanone
- 5,9-dimethyl-2-decanone
- 5-methyl-3-hexen-2-one
- 2-methyl-1-penten-3-ol
- 2-hexanol
- 2-methyl-2-pentanol
- 4-methyl-3-hexanol
- 3-hexanol
- 3-methyl-3-pentanol

Sulfur Containing Compounds
- sulfur, molecular
- sulfonylbis methane
- dimethyl disulfide
- 2-hexanethiol

Other Compounds
- tetrachloroethene

Three columns were obtained and used to analyze the sample by FID and by sniffing. Table 5.2 contains the data from the sniffing and FID runs on all of the columns. The 1-chloroalkane retention times for the intermediate polarity SPB-20 did not differ significantly from the non-polar DB-1 and was therefore not used for the sniffing portion of the experiment. The difference in the retention times on the two columns for geosmin is not great but it is substantial for 2-methylisoborneol. The fact that the retention time stayed nearly the same for geosmin is not of great concern in using this confirmation technique. If the compound detected was not geosmin, it would be unlikely that the retention time would remain the same on the second column. Using the DB-1 sniffing data one can see that the retention times of the odours in the samples closely match those of the geosmin and 2-methylisoborneol standards. When the column was changed to the highly polar DB-WAX column, the sniffing retention times of the menthol odour and the musty odour in the samples, change, to match the retention times of the standards.

After this analysis, the samples were then re-run on the mass spectrometer in the selected ion monitoring mode (SIM). During this run only selected ions of interest were scanned which eliminates most of the data normally collected. This allows the instrument to scan those masses of interest more frequently and greatly improves sensitivity. For geosmin, there are several diagnostic masses that would be indicative of its presence in the sample and these were scanned (m/e 112 (base peak), 97, 125, 126, 149, 167, and the molecular ion 182). Figure 5.4 is the selected ion monitoring scan of the hexane extract of the raw water on 5/6 April 1989 and it clearly indicated the presence of geosmin at a retention time of 27.623 minutes. The retention time of the geosmin standard was 27.635 minutes.

The analogous diagnostic masses for 2-methylisoborneol are m/e 95 (base peak), 108, 150, and the molecular ion, 168. Figure 5.5 is the selected ion monitoring scan of the hexane extract of the raw on the 5/6 April 1989 and it possesses the correct masses with approximately the same relative abundances. This peak elutes at RT 21.112 which is exactly the same as the standard for 2-methylisoborneol.

The hexane extracts of 7/8 April 1989 were then run on the mass spectrometer to determine if these compounds could be detected if the spectrometer was run in full scan mode. Figure 5.6 shows the full mass scan

and extracted ion current profile (EICP) at the expected retention time of geosmin. Although the scan is quite noisy, geosmin is clearly present. The EICP shows the increase in abundance of m/e's 112, 125 and 182 with respect to time. These three diagnostic peaks for geosmin all maximize at the same time giving further proof of the presence of geosmin.

6.3.2 Camphor

In the hexane extracts of the raw water from 5/6 and 7/8 April 1989, a strong library match for camphor was found at RT 22.04. Although the library gave the match a quality of fit rating of 95 (out of 100), no odour of a camphor-like nature was noted at this retention time in any of the solvent extracts. The odour threshold concentration of this compound is a relatively high 1.29 mg/L (van Gemert and Nettenbreijer 1977). This demonstrates the utility of using the GC Sniffing technique in conjunction with GC mass spectrometry as the low OTC compounds present in concentrations too low to be detected by mass spectrometry, such as 2-methylisoborneol, can be detected by the sniffing technique and then the mass spectral method can be optimized to determine the presence of the compound (i.e. selected ion monitoring). Alternatively, the high OTC compounds that may be present in high concentrations, such as camphor, can be detected by the relatively insensitive MSD technique without the use of selected ion monitoring. In a number of the odourgrams however, there was a sour or sour urine odour, that has not been identified, close to the RT for camphor.

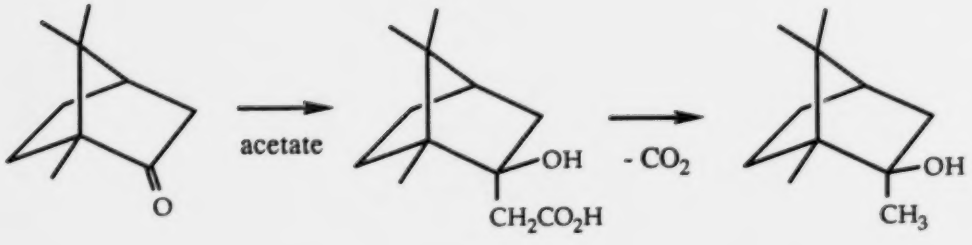
A standard for camphor was obtained and run on the mass spectrometer. Figure 5.7 contains the mass spectrum of the standard compared to the peak that was tentatively identified as camphor in the raw water hexane extract of 7/8 April 1989. The figure clearly shows that both the retention time and the spectrum of the sample closely match those of the standard.

Suffet et al. (1980), concentrated the organics in the raw water supply in Philadelphia using XAD-2 resin and found camphor using GC-MS and suggested it may be 'natural in origin'. Croteau et al. (1981), note that camphor is known to be present in soil and when in the presence of acetate can produce 2-methylisoborneol. They have shown (by tritium labelling) that d-camphor in soil is converted by soil microorganisms to 2-methylisoborneol within 24 hours. Wood and Snoeyink (1977) also note that 2-

methylisoborneol is derived from camphor. A suggested mechanism for this reaction is shown in Figure 6.1.

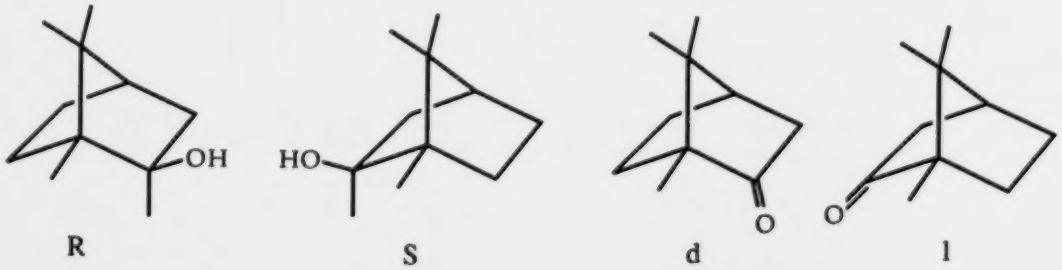
Note that the stereochemistry of the reaction is important as the natural form of 2-methylisoborneol is R, which is derived from d-camphor. As noted in Section 6.3.4.1, stereochemistry plays an important role in odour intensity and quality. Figure 6.2 contains the R and S stereoisomers of 2-methylisoborneol and camphor which are mirror images of each other.

Figure 6.1 Biosynthesis of MIB from Camphor
(after Croteau et al. 1981)



d-Camphor 2-Methylisoborneol

Figure 6.2 R and S Configurations of 2-Methylisoborneol and Precursors



R S d l

2-Methylisoborneol Camphor

6.3.3 Sulfur Compounds

In many of the samples there were very interesting odours that were described as sewer or skunky with some samples containing several such odours (e.g. hexane extracts of raw on 6/7 April 1989). These odours are typical of the sulfur containing compounds such as thiols (R-SH), dimethyl polysulfides and hydrogen sulfide. Many authors have found sulfur containing compounds present in water supplies and they have been implicated in many taste and odour episodes (Wajon et al. (1985a, 1985b), Collins and Gaines (1964), Brownlee et al. (1984), Jenkins et al. (1967) and Gerber (1983)). The odour thresholds of these compounds are very low with some measured in the low ng/L range (e.g. dimethyl trisulfide at 10 ng/L, Mallevialle and Suffet 1987).

It is important to note here the thermal instability of the sulfur compounds which inhibits their isolation by routinely used methodologies. Brownlee et al. (1984) used a micro-extraction with pentane and then reduced the samples with nitrogen prior to GC analysis. Wajon et al. (1985a) found that these compounds could not be determined quantitatively using the standard injection technique of a hot injector port (150°C to 275°C) which vaporizes the sample to facilitate its transport onto the column. They utilized the on-column injection technique whereby the liquid sample is placed directly on the head of the column at relatively low temperatures of 30°C to 50°C. The low boiling sulfur compounds are then rapidly eluted with no thermal degradation as the temperature of the column is ramped up.

Possible evidence for thermal degradation of sulfur compounds was found by the presence of molecular sulfur (S8) in many of the carbon extracts as shown in Figure 5.8. Also, sewer-like odours were noticed in the odourgrams prior to the elution of the relatively low boiling solvents. If these compounds were originally present in the samples prior to analysis they would have been lost in the solvent concentration step where large volumes of solvent were distilled off. An alternative explanation for the presence of the molecular sulfur was that it was present on the original carbon although none was found in the blanks and others have found sulfur in extracts generated by liquid - liquid extraction and XAD resin concentration.

Elemental sulfur has been found in sediment samples from both banks of the river near Devon and through the City of Edmonton at levels of up to 10 mg/g as well as a methoxy substituted disulfide (Anderson et al. 1986). In

addition, samples obtained from Modeste Creek, a tributary of the North Saskatchewan River, contained 3.2 mg/L of sulfur (total) during the 1992 spring runoff (City of Edmonton 1993b). As many of the known sulfur taste and odour causing chemicals have odour threshold concentrations in the µg/L and even ng/L range, these components could contribute to the odour character of the water even if they only constituted a small fraction of the 3.2 mg/L. A number of these compounds have been tentatively identified by mass spectrometry. They include dimethyl disulfide (Figure 5.9), sulfonyl bis methane (Figure 5.10), and hexanethiol (Figure 5.11). The library mass spectral data for dimethyl disulfide was similar to that obtained from the sample with respect to the masses obtained, but not with respect to relative abundances for these masses. This figure has been included as the mass spectrometer conditions with respect to EI voltage and temperature could significantly affect the relative abundances obtained because of the instability of compounds such as dimethyl disulfide.

6.3.4 Other Compounds

Tetrachloroethene was found in the North Saskatchewan River by Anderson et al. (1986) at 0.1 µg/L. This compound is readily adsorbed on GAC and therefore identifying it in the carbon extracts was not surprising. Although it may also be an artifact generated by the solvent as others have found it in dichloromethane, Suffet et al. (1980) identified tetrachloroethene in Philadelphia's finished water and not in the blanks. This compound was found in the hexane extracts from the raw water.

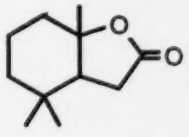
A potent taste and odour causing chemical, 2-isopropyl-3-methoxy pyrazine (IPMP), has been tentatively identified on the basis of odour descriptor and retention time using GC Sniffing. However, mass spectrometric confirmation of the presence of this compound was not obtained.

6.3.4.1 Actinidiolide

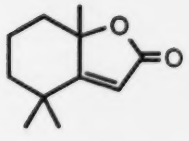
One of the largest peaks routinely obtained in the total ion current chromatograms was 5,6,7,7a-tetrahydro-4,4,7a-trimethyl-2-(4H)-benzo-furanone, which has a common name of dihydroactinidiolide. This lactone (cyclic ester) was found in all of the extracts, raw, treated (with and without PAC) for all solvents (hexane, ethyl acetate and dichloromethane). The

structure of this and related compounds are contained in Figure 6.3. The mass spectra of this compound in the sample (with the excellent library match) can be found in Figure 5.12. This compound was synthesized by Dr. A. Morales and the mass spectrum and retention times were compared to the tentatively identified peak. From this analysis it was determined that the compound was indeed dihydroactinidiolide.

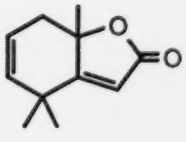
Figure 6.3 Structure of Dihydroactinidiolide and Related Compounds



Tetrahydroactinidiolide



Dihydroactinidiolide



Actinidiolide

Henatsch and Juttner (1983) found that this compound was the dominant compound produced by the cyanobacteria *Synechococcus*. They reported that it produced a pungent violet odour and Suyama et al. (1983) reported that it had a hay-like odour. This compound was also found to be a secretion from the supracaudal (tail) scent gland of the red fox *(Vulpes vulpes)* which has been referred to as the 'violet gland' (Albone 1975).

Although the presence of this compound was confirmed with on the gas chromatography - mass selective detector with a standard, no odour in the odourgrams was noted at the expected retention time. This may be due to the compound possessing a relatively high odour threshold concentration.

In their paper, Henatsch and Juttner (1983) defined dihydroactinidiolide as 2,4,5,7,7a-hexahydro-4,4,7a-trimethylbenzo-furanone (MW 182). However, the structure they provide is inconsistent with this nomenclature (i.e. structure indicates dihydroactinidiolide, MW 180, and IUPAC name indicates tetrahydroactinidiolide, MW 182). A review of the papers cited in Henatsch and Juttner (1983) and others, showed that the IUPAC name for dihydroactinidiolide is actually 5,6,7,7a-hexahydro-4,4,7a-trimethylbenzofuranone, MW 180, which was the compound found in the majority of extracts (Sakan et al. 1967, Isoe et al. 1969, Sanderson et al. 1973, Mori et al. 1990). Additionally, the hexa hydro analog of the above benzofuranone was also found in the hexane extract of April 7/8.

Sakan et al. (1967) reported that dihydroactinidiolide was a component in the essential oil of plants and a physiologically active agent for animals and *Chrysopidae*. They recovered it by dissolving the essential oil of *Actinidia polygama* in hot alkalai and fractionally distilling the mixture. Henatsch and Juttner (1983) found that dihydroactinidiolide was a volatile excretion product of *Synechococcus* (cyanobacteria). They used XAD and Tenax to adsorb this compound. It was removed from the XAD with 20 mL of solvent which was reduced by evaporation in a 'boiling water bath'. The adsorbed material on the Tenax was dried by blowing hydrogen through the column at 100°C for 25 minutes and then desorbing it at 250°C onto the GC.

Lippincott et al. (1990) recovered dihydroactinidiolide in finished drinking water (surface water in New Jersey) using a continuous liquid liquid extractor. This procedure requires that the solvent reservoir be heated so as to volatilize the solvent. The solvent is then condensed and allowed to come into contact with the water, collected in the solvent reservoir and redistilled. For their experiments they extracted 90 L of water in 48 hours. The resulting solvent is then reduced, again with heat, to approximately 2 mL with an automated evaporative concentrator.

Takeoka et al. (1990) recovered 83 volatile components of apricot of which dihydroactinidiolide was obtained at 3 µg/kg. Both of the methods used, headspace analysis and vacuum steam distillation require the input of

heat to the system. The headspace analysis purges the volatiles and they are collected on a Tenax® column, extracted with ether, and reduced with a vigreux column. They note that dihydroactinidiolide is regarded as a carotenoid metabolism product.

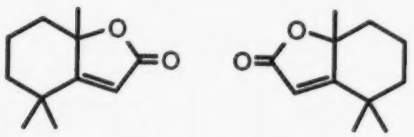
Kanasawud et al. (1990) studied the degradation of ß-carotene in water samples at temperatures ranging from 30°C to 90°C. Carotenoids such as this are widespread in nature from bacteria and fungi to vegetable and animal life. These compounds are highly coloured due to the large number of conjugated double bonds (Allinger et al. 1976). ß-Carotene is a precursor of Vitamin A (Streitwiser and Heathcock 1981), yellow in dilute solutions and in plants, and almost always occurs with chlorophyll (Merck 1989). They identified a large number of compounds, including dihydroactinidiolide, after heating ß-carotene for short periods of time. They showed that dihydroactinidiolide is the first compound produced from the heat treatment of ß-carotene and it was the largest compound produced at all temperatures. At 30°C, only dihydroactinidiolide was produced. The results that they obtained in water confirm the results of others (as cited in their paper) who studied the degradation of ß-carotene in organic solvents.

Sanderson and Graham (1973) also showed the oxidation of ß-carotene to dihydroactinidiolide and other compounds arising from tea leaves. They note that each step of the processing of tea decreased the concentration of ß-carotene. This was reasonable due to the highly reactive conjugated double bonds present in carotene and in the presence of oxidizing agents will react at these bonds. Kanasawud et al. (1990) also showed this when they studied the degradation of ß-carotene with and without oxygen. The results indicate the degradation and resulting formation of dihydroactinidiolide proceeds much more rapidly in the presence of oxygen. Isoe et al. (1969) showed that ß-carotene could be photo-oxygenated to produce ß-ionone and dihydroactinidiolide without heat.

After dihydroactinidiolide was synthesized and made available it was analyzed by GC sniffing analysis but there was no odour at the expected retention time. Mosandl et al. (1989a, 1989b) note that lactone enantiomers exhibit differences in odour quality as well as intensity based on geometric isomerism and chirality respectively. Dihydroactinidiolide exists in two forms, R and S (Figure 6.4). It is possible that one of the stereoisomers is odorous (naturally occurring) and the other is not (perhaps the one produced

synthetically). Guichard et al. (1990) demonstrated that in nature, the R enantiomer always predominated when analyzing lactones and noted that the optical purity is an important part of the aroma of natural products. Monsandl et al. (1989b), Guichard et al. (1990), and Schomburg et al. (1984) have developed methods to separate the enantiomers in their investigations of odour character in natural products.

Figure 6.4 Enantiomeric Forms of Dihydroactinidiolide



R S

Another example of odour dependent isomerism is geosmin. This compound can exist in four forms, cis/trans, cis/cis, trans/cis and trans/trans with the latter being the compound found in nature. These compounds have been synthesized and their sensory properties were evaluated by Maga (1987). It was found that the cis/trans and trans/trans had a very pungent earthy/musty odour. Conversely, the trans/cis and cis/cis isomers only had a slight earthy odour and was reminiscent of camphor and cedar.

6.3.4.2 Aldehydes

Although some aldehydes were found, it was not unexpected to find so few given the inputs as noted by Hrudey et al. (1988a). First, aldehydes are poorly removed from potable water supplies by GAC and low recoveries of low levels can be expected. The methods used to detect the aldehydes (FID and MSD) are very insensitive and a derivatizing method should be used (Sclimenti et al. 1990) to reliably detect them.

Hrudey et al. (1988b), have shown that amino acids would react with disinfectants to form odorous aldehydes with relatively low odour threshold concentrations. Grov et al. (1963a, 1963b, 1963c) have shown that these amino acids are present in soils and could therefore be leached out into surface water supplies.

Several aldehyde compounds were tentatively identified (with fair matches) from the mass spectra of the extracts. Two of these compounds provided odours at the correct retention times in the odourgrams. The first, 3,7-dimethyl-7-octenal, came at the same retention time as a sweatsock odour in the odourgram and the second, 2-methyl-2-pentenal had a rotting odour in the odourgram. The former is a natural product also known as alpha citronella. Juttner et al. (1986) identified the latter compound in lake water during a cyanobacterial bloom and during the development of spring phytoplankton in southwest Germany. The mass spectral data for these compounds are presented in Figures 5.13 and 5.14.

The presence of benzaldehyde was confirmed with the mass spectrometer and a commercially available standard. The mass spectral data for this compound can be found in Figure 5.15. This compound is reported to have an almond odour (Merck 1989) and an almond odour was noted at the proper retention time in the odourgrams. The odour threshold concentration of this compound is reported to be 3 µg/L (Bartels et al. 1989). Chriswell et al. (1977) found that GAC recovered only 2% of the loaded benzaldehyde which suggests that the concentrations in the original water samples was much larger than that recovered from the carbon. A derivative of this compound, hydroxy benzaldehyde, was also found in the extracts with the characteristic bitter almond odour. Gerber (1983) has also isolated 2-hydroxybenzaldehyde, which is commonly known as salicyaldehyde, in odorous waters where actinomycetes were thought to be the cause of the odour problem.

6.3.4.3 Cineole

Cineole has frequently been found in surface water supplies (Khiari 1992, Suffet 1980). Merck (1989) notes that this compound has a camphor-like odour with a spicy cooling taste. The odour threshold concentration of this compound is approximately 12 µg/L (Fazzalari 1978). This compound, also referred to as eucalyptol, was found in the mass spectral data obtained on the

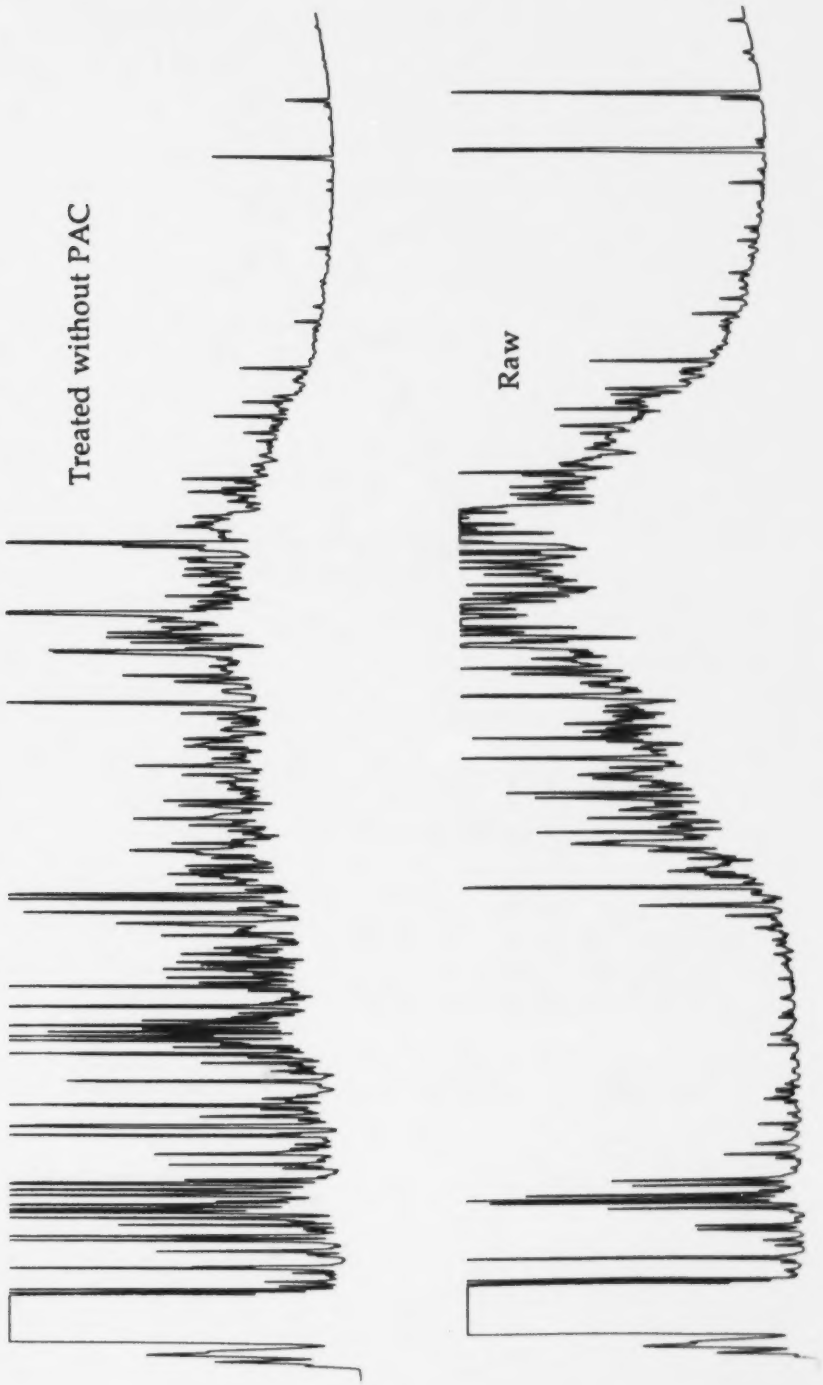
MSD as well as from a more sensitive high resolution instrument. The mass spectra from these runs can be found in Figure 5.16. At the expected retention time in the odourgrams, only a strong marijuana odour was noted in the hexane extract of April 4/5.

6.4 Effect of PAC and Disinfection on Taste and Odour

Figure 6.5 contains the GC traces for the raw and treated without PAC dichloromethane extracts from April 4/5 1989. These traces show the effects of the treatment process on the relative molecular size (as column separates primarily on size) and concentration (as measured by area counts) of the components in the water. The pilot plant attempted to mimic the EL Smith WTP and so the process consisted of alum, ammonia and polymer addition followed by disinfection with chlorine dioxide and chloramines. In the raw water extract, there was a large mass of unresolved organics which is significantly reduced in the treated water extract. In the treated water extracts, there were many large peaks between in the early portions of the chromatograms that were not present in the raw water extracts. As the column separated components primarily by size, the increase in peaks of lower retention time indicated an increase in the number of lower molecular weight compounds. The larger compounds were likely oxidized and fragmented by the disinfectant chlorine dioxide. As previously noted, the action of the disinfectant can lead to the formation of taste and odour compounds. However, in the odourgrams contained in Table 5.5, the number of peaks and the descriptors remained relatively the same indicating that those compounds associated with the peaks of low retention time in the treated water extract were not responsible for the odour character of the extract. In fact, the odourgrams for the raw and treated extracts are remarkably similar throughout which indicated that chlorine dioxide was ineffective in the removal of the odorous compounds. Note that this assumes that the compounds associated with Edmonton's taste and odour problem were successfully recovered and noted in the odourgram.

The hexane extracts from the same day indicate a similar phenomenon with the raw water extracts possessing a large hump between 25 and 45 minutes indicating the presence of unresolved large molecular weight organics. The corresponding treated water extracts did not have the hump but they also did not have any increase in the number or size of lower

Figure 6.5 Effect of Disinfection on Organic Compounds by FID



molecular weight compounds. The difference between the hexane and dichloromethane extract chromatograms was likely due to differences in solvent polarity. Non-polar hexane can be expected to extract non-polar solutes whereas intermediate polarity dichloromethane will extract more polar solutes. The low molecular weight compounds formed by the disinfection process will be more polar because of the greater influence of polar functional groups and chlorine/oxychlorine substitution.

In contrast to the differences in chromatograms, the raw water odourgram (Table B.4), shows marked differences to the treated water odourgrams in the hexane extracts. The raw water extract contains 56 odours while the treated water sample contains only 25 odours. Figure 5.1 graphically compares the odourgrams of these extracts and it can be readily seen that the raw extract has many more peaks throughout the odourgram.

The above discussion indicates that the presence or absence of peaks in the FID trace has no relation to the presence or absence of odours in the odourgram. Figure 6.6 compares an odourgram and a chromatogram from a raw water extract. As can be seen in the figure, the larger peaks in the chromatogram generally produce little or no odour. This was also noted by Savenhed et al. (1985) who found that the most odorous peaks found were in the 'grass' or noise of the chromatogram. Many of the compounds that have been found to cause taste and odour problems in finished drinking water have odour threshold concentrations in the ng/L range whereas the components present in the largest concentrations have little or no odour.

In many of the chromatograms, there was a reduction in number and intensity of peaks with the addition of PAC. In the hexane extracts of 5/6 April 1989, the camphor-like odour due to 2-methylisoborneol is in the raw and treated without PAC but removed in the treated with PAC. The musty earthy odour characteristic of geosmin was reduced from strong to medium intensity and the odour character became swampy with PAC addition. The number of odours detected also changed significantly upon the addition of PAC. In the raw, there were 34 odours and in the treated there were 41. The PAC treated water only contained 19 odours.

Figure 6.7 compares the results for the GC-Sniffing experiments for the hexane extract of 5/6 April 1989. The impact of disinfection and PAC treatment is clearly shown with the majority of peaks being removed by the PAC and disinfection having little impact. Of the four major peaks, one was

Figure 6.6 Odourgram and FID Chromatogram Comparison

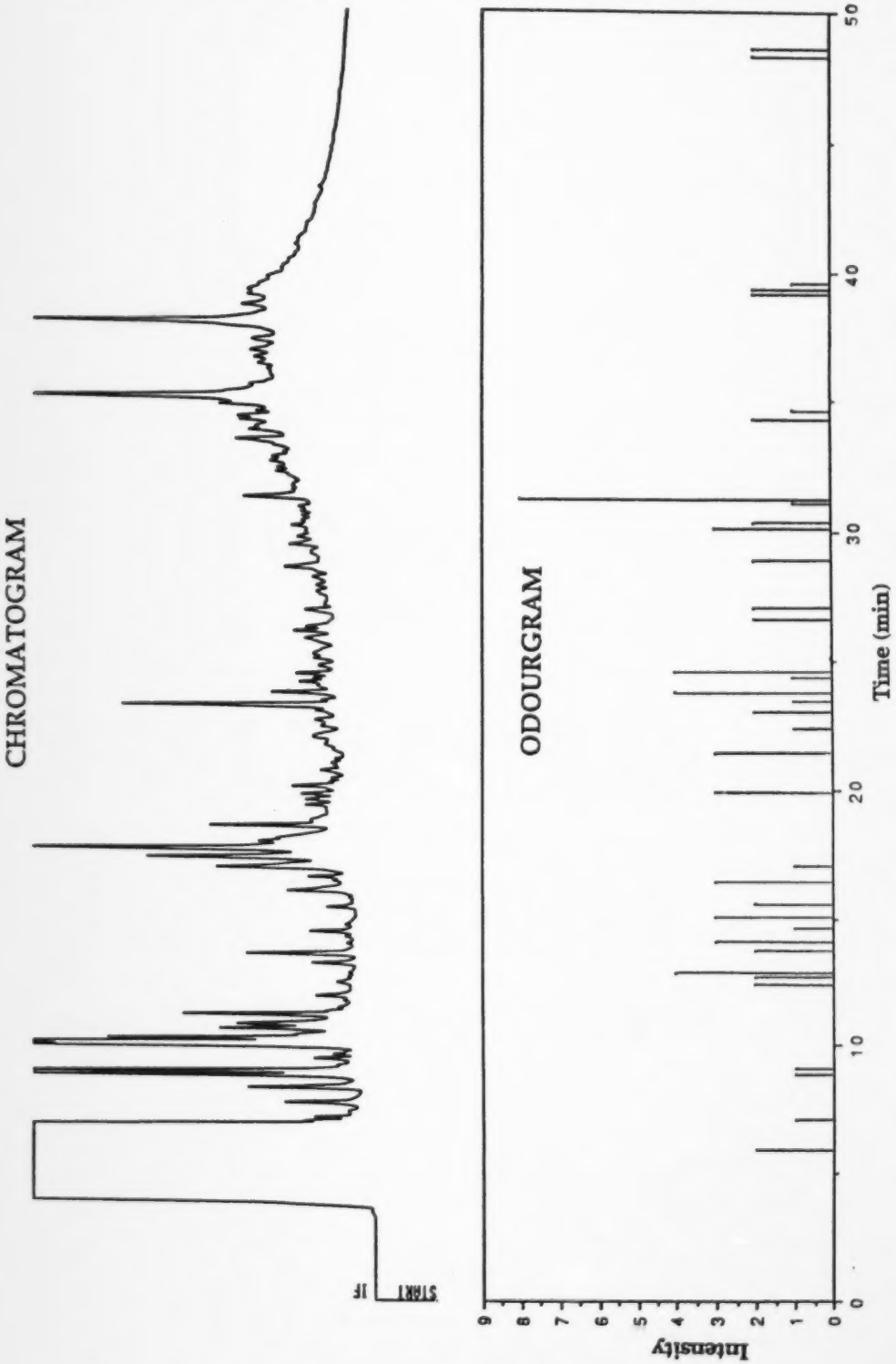
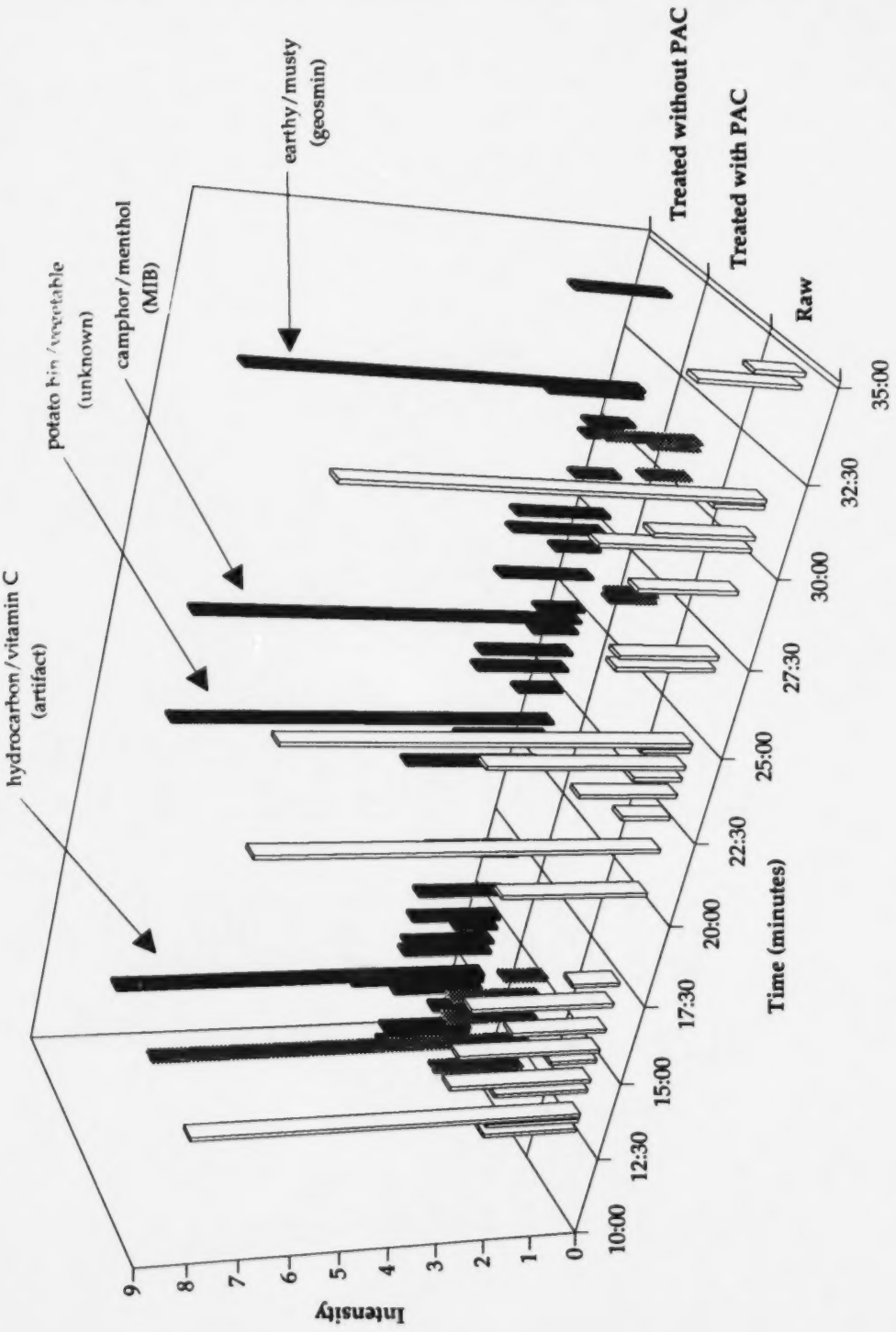


Figure 6.7 Odourgrams of Raw and Treated Hexane Extracts



identified as a method artifact (RT 12.46), one as MIB (RT 24.30), and another as geosmin (RT 31.20). The final major peak at RT 21.24 possessed a potato bin/vegetable/garden odour in many of the extracts. This odour is characteristic of 2-isopropyl-3-methoxy pyrazine (IPMP). Evidence for the presence of this compound included the odour descriptor and retention time by GC-Sniffing. However, mass spectrometric evidence was not obtained.

6.5 Comparison of Carbon Extract and 60 L Extract

The two traditional methods for the concentration of organics in water are liquid-liquid extraction and liquid-solid extraction with sorbents. Both methods employ a significant amount of sample workup and they are reviewed in Section 2.2.1. Advantages of using sorbents are that less solvent is generated that must be reduced and higher concentration factors are possible because of increased sample volumes. Typically, sorbents are used to extract 100 litres to 2000 litres whereas solvent extractions use only 4 litres to 60 litres as each litre must be manually extracted. Problems with the sorbents are incomplete adsorption and/or desorption which are compound specific. Those compounds that are well adsorbed are difficult to recover as was the case with geosmin which was incompletely recovered after successive extractions with three different solvents of varying polarity.

Table B.13 contains the sniffing data comparing the hexane extracts from 5/6 April and the 60 litres dichloromethane extraction (acid extract). The hexane extract was used for this comparison as it was the first solvent used and contained the most peaks. Similarly the base extract was not used as the acid extract was completed first. As noted above, the raw, treated with PAC and treated without PAC contained 34, 19 and 41 odours respectively. The acid extract contained 64 odours with more interesting descriptors such as flowery, piney forest, mushrooms and rotting. Geosmin was found in all 4 samples at a retention time of approximately 31.20 minutes. The geosmin odour in the 60 L extract was very strong with a piney forest descriptor. 2-Methylisoborneol was also believed to be present in the 60 litres extract as a chemical odour was detected at the correct retention time.

7.0 Conclusions

1. The spring odour character of the City of Edmonton's raw and treated water was shown to be very complex and composed of at least geosmin, 2-methylisoborneol, other terpenoid compounds, aldehydes and sulfur containing compounds.

2. The presence of geosmin and 2-methylisoborneol was shown in the City of Edmonton's raw water in the spring of 1989. Because of limitations of the method used to concentrate the organics in the water the actual level could not be accurately determined. Their presence however, is certainly in excess of 1 ng/L for geosmin and 1 ng/L for 2-methylisoborneol. These levels should be considered conservative (i.e. low) for the following reasons.

- Water flow to the carbon cartridges was interrupted (especially for the raw water) and calculations of nominal concentrations of these odorous compounds were determined on the basis of a nominal flow of 2000 L.
- The techniques used to recover and concentrate these compounds have severe limitations when dealing with volatile and semi-volatile compounds. Significant losses are possible because of incomplete adsorption onto the carbon, incomplete desorption from the carbon and loss of volatiles during solvent concentration.
- Incomplete desorption of geosmin was noted in all of the samples as it was found in successive extractions of the same carbon with different solvents.

3. GC-Sniffing was shown to be an effective tool for detecting odorous components of raw and treated water so that efforts to determine their identity can be focused, without pursuing the futile task of having to identify all of the compounds present in the samples. Unlike the FID, the human sensor selectively discriminates between those compounds present at high concentrations with high OTC's and those present at low concentrations with low OTC's.

4. Concentrating organic compounds on granular activated carbon and removing and concentrating them by Soxhlet extraction and Kuderna Danish evaporation was found to be too harsh a procedure for the reliable determination of taste and odour compounds. During these procedures, compounds are lost due to their high volatility or decomposition. Other compounds are likely formed from the decomposition of larger molecules which can then interfere with the determination of the taste and odour compounds originally present in a water sample.

5. The use of the preparative GC method for the concentration of odorous compounds was shown to be ineffective (as used in this work) due to poor recoveries of the compounds of interest.

6. Powdered activated carbon was effective in removing the odours associated with 2-methylisoborneol and the tentatively identified 2-isopropyl-3-methoxy pyrazine. PAC was found to be less effective for the removal of geosmin.

8.0 Recommendations

1. One of the major problems in using granular activated carbon (GAC) to concentrate organics is the blank problem. In order to prevent contamination of the samples with artifacts, one can wash the carbon with solvent until the extracts are clean. Alternatively, one can employ a system blank using virgin carbon and account for all the artifacts in the sample.

Both of these solutions have their drawbacks. By allowing the artifacts to contaminate the sample, there is a danger that some of the sample peaks may be lost in the clutter of artifacts. If the GAC is washed with a solvent prior to use, there is the danger that some of the adsorption sites on the GAC could be taken up by some of the solvent. This problem could be partially alleviated by re-activating the GAC by placing it in an oven at an elevated temperature to drive off the residual solvent. However, a previous study showed that even after thermally desorbing GAC preloaded with trihalomethanes (THM's) at 250°C, additional recoveries were observed when the same GAC was desorbed at 350°C. This was especially true for the highest molecular weight THM, bromoform, where more was recovered at the higher temperature.

Consequently, isotherms should be performed on virgin and solvent washed GAC to determine if the adsorptive capacity of the washed GAC is reduced. The kinetics of this adsorption is also very important as the most active sites may be taken up by the solvent and thereby significantly lengthen the time required for adsorption on the less active sites. Therefore a kinetic study of the washed and unwashed carbons should also be performed.

The chemicals used for these experiments could be geosmin, 2-methylisoborneol, isobutylmethoxypyrazine, isopropylmethoxypyrazine, ß-cyclocitral, 2,3,6-trichloroanisole, 2,4,6-trichloroanisole and cis-3-hexen-1-ol, all of which are readily available and are known taste and odour causing compounds.

2. Another problem area in the use of sorbents to concentrate organics relates to the recoveries (both adsorption and desorption) of various compounds by the sorbent. As the cartridges are essentially mini-columns, laboratory studies can be performed by passing water spiked with various components (as in 1 above) and both the solid and the liquid phases analyzed

for them. This would provide information on the absolute recoveries possible on the sorbent which can then be used to calculate a more accurate concentration for the components. It would also indicate the efficiencies of both adsorption and desorption. This test could also be used to determine the optimum flow rate to recover the maximum amount of the components.

3. Artifacts generated by the solvent can also be a very significant problem. Ethyl acetate was found to generate a large number of carboxylic acids and esters which covered large portions of the chromatograms even though several studies indicate it to be a superior solvent for extractions. Therefore, a solvent with a similar dielectric constant (i.e. polarity) should be found for future work.

4. Other sorbents such as the XAD macro-reticular resins should also be evaluated either singly or in combination to obtain a more complete picture of the organic compounds in the water. One study showed that the XAD-2 resin preferentially adsorbs humic acid and used it in combination with another resin and carbon. This has the potential to use XAD resin as a pre-filter thereby preventing the carbon or another resin from being fouled with humics materials. This might measurably clean up the resulting chromatograms.

5. Losses of some of the more volatile compounds during the Soxhlet and evaporation stages are unavoidable. One method that could be employed to analyze for these compounds is the use of thermal desorption to desorb the adsorbed organics off of the preloaded carbon samples. This method has been employed by others in the analysis of low molecular weight aldehydes and trihalomethanes. This would be an extremely powerful technique in the analysis of volatile sorbed organics especially when employed with GC-MS or GC-sniffing. By using this method one eliminates the two steps where the majority of the losses occur as well as minimizing the sample work up (although the carbon may have to be dewatered, crushed and sieved prior to analysis). This method would provide a water extract volume onto the gas chromatograph better than that of CLSA (e.g. 2000 L of water over 100 grams of carbon provides 20 L of water per gram. 0.1 grams of carbon desorbed onto the gas chromatograph would be equivalent to 2 L of water. Similar

calculations for CLSA indicate that only 80 mL to 320 mL of water extract are injected onto the gas chromatograph).

6. The results of this research have shown the presence of sulfur and some unidentified sulfur containing compounds. As some of the taste and odour episodes experienced in Edmonton had a 'sewer like' smell and sulfur containing compounds such as dimethyltrisulfide, hydrogen sulfide and mercaptans are extremely odorous, the analytical techniques for these compounds should be investigated and optimized. This is critical as many researchers have found that the normal techniques used to analyze for these compounds were much too harsh as the compounds were very reactive and thermally labile (subject to decomposition with the addition of heat).

7. The recoveries obtained from the freezing out portion of this work were unacceptable. As others have been able to achieve recoveries over 80%, the differences between methodologies were analyzed. The only apparent difference was the use of another GC fitted with an on-column injection port for all quantitation. This would eliminate the decomposition in the injector port. It is therefore recommended that for future work another GC with such a injection port be used. This would also have the added advantage of reducing the down time due to 1) the switching of the GC back and forth from freezing to quantitation, 2) the inevitable breakdowns and problems this switching causes and 3) aid in determining exactly where the losses were actually occurring.

8. Much of the preparative style work performed with natural products is done with much larger quantities (milligram to gram quantities). In this work, packed columns with their much higher loading capacities, are used to fractionate and concentrate the compounds of interest. The collected fraction can be collected on an adsorbent or a piece of capillary column at ambient temperature. With the advent of zero-dead space capillary connectors, the small piece of the capillary column can be fitted directly to another instrument (GC or MSD) and the sample analyzed. Larger volumes of sample could also be injected (up to 250 µL) which would increase the amount of analyte collected during each run. It is recommended that some of the

remaining samples could be combined for just such a procedure and the identity of the unknown components be determined.

9. In order to obtain a greater concentration of analyte, a large number of samples that were extracted and not analyzed could be combined and separated by gel chromatography. The resulting fractions could be sniffed and the odours that have been unidentified (such as the vegetable odour) focussed upon using mass spectrometry.

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Appendix A - Sources of Taste and Odour

Table A.1 Taste and Odour Compounds Produced by Actinomycetes

Compound	Odour Descriptor	OTC (mg/L)	Reference
acetaldehyde		0.015	Dougherty et al. 1966
acetic acid	vinegar	0.007	Dougherty et al. 1966
ammonia	sharp pungent	0.037	Dougherty et al. 1966
butyric acid	rancid	0.001	Weete et al. 1979
cadin-4-ene-1-ol	woody earthy		Mallevialle and Suffet 1987
cadin-4-ene-1-ol	earthy woody		Gerber 1979
ethyl alcohol		0.25	Dougherty et al. 1966
furfural	putrid	0.006	Gerber 1983
geosmin	earthy musty	0.000004	Gerber et al. 1965
hydrogen sulfide	rotten egg	0.0011	Collins et al. 1964
isobutyl acetate		0.004	Dougherty et al. 1966
isobutyl alcohol	sweet musty	0.12	Dougherty et al. 1966
2-isopropyl-3-methoxy pyrazine	potato bin	0.000002	Gerber 1979
5-methyl-3-heptanone	sweet		Gerber 1979
2-methylisoborneol	musty camphor	0.000009	Medsker et al. 1969
octan-3-one	estery		Gerber 1983
phenol-3-octanone			Cross 1981
1-phenyl-2-propanone			Gerber 1979
2-phenylethanol		1.45	Cross 1981
ß-phenylethyl acetate	chrysanthenum		Weete et al. 1979
salicyaldehyde	phenolic spicy		Cross 1981

Table A.2 Taste and Odour Compounds Produced by Algae

Compound	Odour Descriptor	OTC (mg/L)	Reference
acetaldehyde		0.015	Juttner 1983
acetone	sweet fruity	1.29	Mohren et al. 1983
1-aminopropane		90.1	Herrmann et al. 1977
2-aminopropane			Herrmann et al. 1977
bromophenols	iodine	0.0001	Mallevialle and Suffet 1987
butan-2-one	ethereal	50	Mohren et al. 1983
butanolamine			Herrmann et al. 1977
butanone	ethereal	50	Juttner 1983
butyl mercaptan		0.001	Jenkins et al. 1967
camphene			Juttner 1983
carene, delta			Juttner 1983
p-cresol	medicinal chemical	0.044	Mallevialle and Suffet 1987
ß-cyclocitral	smoky tobacco	0.0193	Hayes et al. 1989
cyclocitral, alpha	musty cut grass		Juttner 1988
cyclocitral, beta	tobacco green	0.0193	Persson et al. 1983, Juttner 1988
p-cymene	weak citrus		Juttner 1983
2,4-decadienal	cod liver oil, rancid	0.00007	Hayes et al. 1989
diacetone alcohol	sweet	0.28	Juttner 1983
p-dichlorobenzene		0.0003	Mallevialle and Suffet 1987
1,2-dihydro-1,1,6-trimethylnaphthalene			Juttner 1983
dimethyl disulfide	foul putrid	0.0012	Jenkins et al. 1967, Hayes et al. 1989
dimethyl pentasulfide			Brownlee et al. 1984
dimethyl sulfoxide			Juttner 1988
dimethylsulfide	fishy	0.003	Jenkins et al. 1967
dimethyltetrasulfide	foul putrid		Brownlee et al. 1984, Hayes et al. 1989
dimethyltrisulfide	foul putrid, swampy	0.00001	Jenkins et al. 1967, Hayes et al. 1989
elemental sulfur			Brownlee et al. 1984
ethanol	sweet	0.25	Juttner 1983
ethanolamine			Herrmann et al. 1977
ethyl acetate	sweet ester	0.257	Juttner 1983
ethyl propanoate	sweet fruity	0.000006	Juttner 1983
farnesol	lilac floral		Juttner 1983
formaldehyde		0.8	Juttner 1983
furfuraldehyde	sweet fragrant		Juttner 1983
geosmin	earthy musty	0.000004	Safferman et al. 1967
germacrene-D	unpleasant grassy		Hayes et al. 1989
2,4-heptadienal	cod liver oil		Hayes et al. 1989
heptan-2-ol	earthy oily	0.003	Juttner 1983
heptan-2-one	spicy cinnamon	0.14	Juttner 1983

Table A.2 (cont'd) Taste and Odour Compounds Produced by Algae

Compound	Odour Descriptor	OTC (mg/L)	Reference
heptan-3-one	fruity green sweet	0.0075	Juttner 1983
heptanal	fishy oily woody	0.003	Mallevialle and Suffet 1987
hex-1-en-3-ol	green fresh grass	0.00025	Juttner 1988
hexan-3-one	ethereal grape wine		Juttner 1983
hexanal	old grass	0.0045	Mallevialle and Suffet 1987
hexanol	fruity	0.01	Hayes et al. 1989
2-hydroxy-2,6,6-trimethylhexanone			Juttner 1988
indole	fecal musty	0.3	Mallevialle and Suffet 1987
ionone, alpha	violet	0.0938	Juttner 1988
ionone, beta	fragrant sweet	0.000007	Juttner 1988
isobutylmercaptan			Jenkins et al. 1967
isopropyl mercaptan	onion		Jenkins et al. 1967
limonene	lemon orange	0.004	Juttner 1983
methyl butanone			Juttner 1983
methyl ethanethiolate			Juttner 1983
methyl geraniate			Juttner 1983
methyl hexadecanoate			Mallevialle and Suffet 1987
3-methyl indole	fecal nauseating	0.0012	Brownlee et al. 1984
methyl mercaptan		0.00002	Jenkins et al. 1967
methyl methylpropanoate			Juttner 1983
methyl propanethiolate			Juttner 1983
methyl propanoate			Juttner 1983
3-methyl-1-butanol	fuel oil		Hayes et al. 1989
methyl-2-methylbutanoate			Juttner 1983
methyl-2-methylpropanethiolate			Juttner 1983
methyl-2-methylpropanoate			Juttner 1983
methyl-3-methylbutanethiolate			Juttner 1983
6-methyl-5-hepten-2-one	fruity ester		Hayes et al. 1989
methyl-9-octadecanoic			Mallevialle and Suffet 1987
methylamine		0.65	Herrmann et al. 1977
2-methylbut-2-en-1-ol			Juttner 1983
3-methylbutan-1-ol		0.25	Juttner 1983
3-methylbutyl acetate		0.005	Juttner 1983
6-methylhept-5-en-2-one			Juttner 1983
6-methylhept-5-en-2-one			Juttner 1988
6-methylheptan-2-one			Juttner 1988
2-methylisoborneol	musty camphor	0.000009	Tabachek et al. 1976
methylmercaptan	rotten cabbage	0.00002	Jenkins et al. 1967
2-methylpent-2-enal	rhum marzipan	0.29	Persson et al. 1983
methylpent-3-one			Juttner 1983
methylpropan-1-ol		3	Juttner 1983
2-methylpropyl acetate			Juttner 1983

Table A.2 (cont'd) Taste and Odour Compounds Produced by Algae

Compound	Odour Descriptor	OTC (mg/L)	Reference
5-methylthio-1,2,3-trithiane			Juttner 1983
4-methylthio-1,2-dithiolane			Juttner 1983
myrcene	pleasant		Juttner 1983
naphthalene		0.0068	Mallevialle and Suffet 1987
2,6-nonadienal	cucumber		Hayes et al. 1989
oct-1-en-3-ol	chantarelle musty		Mohren et al. 1983
oct-2-en-1-ol	rancid		Mohren et al. 1983
octa-1,3-diene	mushroom humus	5.6	Persson et al. 1983
octa-1,5-dien-3-ol			Mohren et al. 1983
octa-1-trans-3-cis-5-triene			Mohren et al. 1983
1,3-octadiene			Juttner 1983
octan-1-ol	oily rancid	0.13	Juttner 1983
1,3,5-octatriene			Juttner 1988
octatriene			Juttner 1983
octen-1-en-3-ol	chantarelle musty		Juttner 1983
pentan-2-one	sweet fruity	70	Juttner 1983
pentan-3-one			Juttner 1983
pentanal		0.012	Juttner 1983
phellandrene, beta			Juttner 1983
phenyl ethanol	floral roses	1.45	Hayes et al. 1989
2-phenylethanol			Juttner 1983
pinene, alpha	woody turpentine	0.0025	Juttner 1983
pinene, beta		0.14	Juttner 1983
propan-2-ol			Juttner 1983
2-propyl acetate	celery sweet ester	0.05	Juttner 1983
propyl acetate			Juttner 1983
putrescine	strong piperidine	22	Mallevialle and Suffet 1987
trans-geranylacetone		0.06	Juttner 1983
transcisdeca-2,4-dienal		0.00007	Juttner 1983
trimethylamine	fishy	0.000367	Herrmann et al. 1977
2,6,6-trimethylcyclohex-2-en-1-one	woody tobacco	0.42	Juttner 1988
2,2,6-trimethylcyclohexanone	tobacco	0.31	Juttner 1988
trimethylcyclohexanone	tobacco	0.31	Persson et al. 1983
1,3,3-trimethylcyclohexene			Juttner 1988
trimethylcyclohexene	tobacco	7.1	Persson et al. 1983
trimethylcyclohexenone	tobacco potato cellar	0.42	Persson et al. 1983
1,2,4-trithiolane			Juttner 1983
xylene all isomers	sweet solvent	0.02	Mallevialle and Suffet 1987

Table A.3 Taste and Odour Compounds Produced by Other Organisms

Compound	Source	Odour Descriptor	OTC (mg/L)	Reference
dimethyl polysulfides	bacteria	swampy	0.00001	Wajon et al. 1985a
geosmin	fungi	earthy	0.000004	Mallevialle and Suffet 1987
geosmin	fungi	musty		Kikuchi et al. 1981
hydrogen sulfide	bacteria	rotten egg	0.0011	Mallevialle and Suffet 1987
methyl mercaptan	bacteria	decayed cabbage	0.0011	Mallevialle and Suffet 1987
6-pentyl-alpha-pyrone	fungi			Kikuchi et al. 1981
phenylacetaldehyde	fungi	harsh hawthorn	0.004	Kikuchi et al. 1981
2-phenylethanol	fungi	floral rose		Kikuchi et al. 1981
toluene	bacteria	woody chemical	0.14	Juttner 1988

Table A.4 Taste and Odour Compounds from Abiotic Sources

Compound	Odour Descriptor	OTC (mg/L)	Reference
1,4-dichlorobenzene	penetrating	0.0003	Mallevialle and Suffet 1987
2,3,6-trichloroanisole	muddy camphor	0.0000001	Mallevialle and Suffet 1987
2,4,6-trichlorophenol	phenolic	0.94	Kovacs et al. 1984
2,4-dichlorophenol	medicinal	0.056	Kovacs et al. 1984
2-chlorophenol		0.00012	Kovacs et al. 1984
2-methyl-5-ethylpyridine	sour pungent	0.006	Cees et al. 1974
2-methylbenzthiazole		0.0075	Cees et al. 1974
aldrin	musty mouldy	0.017	Sigworth et al. 1965
benzene	sweet	2	Mallevialle and Suffet 1987
benzene hexachloride, delta	musty	0.00013	Sigworth et al. 1965
bis(2-chloroisopropyl)ether		0.2	Cees et al. 1974
carbon tetrachloride		0.2	Mallevialle and Suffet 1987
chlordane	musty	0.00032	Sigworth et al. 1965
dichlorobenzenes	sweet muddy	0.01	Cees et al. 1974
dichloroisopropylether		0.017	Cees et al. 1974
ethylbenzene	sweet	0.14	Cees et al. 1974
gasoline	chemical	0.01	Mallevialle and Suffet 1987
guaiacol	burnt woody	0.02	Kovacs et al. 1984
hexachlorobutadiene		0.006	Cees et al. 1974
isobutyl acetate	sweet ester	0.073	Mallevialle and Suffet 1987
naphthalene		0.0005	Cees et al. 1974
oil	hydrocarbon	0.0005	Mallevialle and Suffet 1987
phenylmethylcarbinol		1.45	Cees et al. 1974
polychloroanisoles	musty	0.0004	Paasivirta et al. 1987
polychlorocymenes			Paasivirta et al. 1983
polychlorophenols		0.00012	Paasivirta et al. 1983
polychloroveratroles	woody		Paasivirta et al. 1987
tert-butylbenzene	aromatic	0.0005	Mallevialle and Suffet 1987
tetrachloroethylene	ethereal	0.3	Mallevialle and Suffet 1987
tetralin	benzene menthol		Cees et al. 1974
trichloroethylene	solvent	0.5	Mallevialle and Suffet 1987
xylenes	sweet chemical	0.02-1.8	Mallevialle and Suffet 1987

Table A.5 Taste and Odour Compounds Produced During Treatment

Compound	Odour Descriptor	OTC (mg/L)	Reference
acetaldehyde	pungent	0.015	Glaze et al. 1989
aldehydes*			Anselme et al. 1985a
aliphatic aldehydes			Mallevialle and Suffet 1987
alkyl naphthalene*			Anselme et al. 1985a
alkyl thiophene*			Anselme et al. 1985a
anisole	aromatic	0.05	Mallevialle and Suffet 1987
aromatic aldehydes			Mallevialle and Suffet 1987
benzaldehyde	fruity	0.00018	Anselme et al. 1988
benzene derivatives*			Mallevialle and Suffet 1987
bromoform	medicinal	0.3	Mallevialle and Suffet 1987
carboxylic acids			Glaze et al. 1989
chloramines	chlorine		Mallevialle and Suffet 1987
chlorine	chlorine		Mallevialle and Suffet 1987
chloroanisoles			Mallevialle and Suffet 1987
chloroform		0.1	Mallevialle and Suffet 1987
2-chlorophenol	medicinal	0.0002	Mallevialle and Suffet 1987
decanal	citrus	0.0001	Mallevialle and Suffet 1987
decanal	citrus	0.0001	Glaze et al. 1989
1,5-di-t-butyl-3,7-dimethyl bicyclohexan-2-one*			Anselme et al. 1985a
dichloramine	swimming pool	0.15	Krasner et al. 1984
2,4-dichlorophenol	medicinal	0.002	Mallevialle and Suffet 1987
2,6-dichlorophenol	medicinal		Mallevialle and Suffet 1987
4-chlorophenol	medicinal	0.0005	Mallevialle and Suffet 1987
6,10-dimethyl-5-9-undecadiene-2-one		0.06	Glaze et al. 1989
dimethylpolysulfides			Mallevialle and Suffet 1987
dimethyltrisulfide*	swampy garlic	0.00001	Wajon et al. 1985
1,3-dioldiisobutyrate*			Anselme et al. 1985a
4-ethyl-2,6-di-t-butyl phenol*			Anselme et al. 1985a
formaldehyde	pungent	0.8	Glaze et al. 1989
heptanal	oily rancid	0.003	Anselme et al. 1988
heptanal	oily rancid	0.003	Glaze et al. 1989
hydrogen sulfide	rotten egg	0.0011	Mallevialle and Suffet 1987
hypochlorite ion	chlorinous	0.36	Krasner et al. 1984
hypochlorous acid	chlorinous	0.28	Krasner et al. 1984
iodoform	medicinal	0.00002	Mallevialle and Suffet 1987
iodoform	medicinal	0.00002	Hansson et al. 1987
ketones*			Anselme et al. 1985a
methyl ethyl ketone*	sweet sharp	2	Mallevialle and Suffet 1987
4-methyl-2,6-di-t-butyl phenol*	plastic		Anselme et al. 1985a

Table A.5 (cont'd) Taste and Odour Compounds Produced During Treatment

Compound	Odour Descriptor	OTC (mg/L)	Reference
4-methyl-2,6-di-t-butylphenol*	burnt plastic		Mallevialle and Suffet 1987
2-methylbutanal		0.0125	Hrudey et al. 1988b
3-methylbutanal	sickening sharp	0.0002	Hrudey et al. 1988b
2-methylpropanal		0.001	Hrudey et al. 1988b
methylisobutyl ketone*	sweet sharp	0.01	Mallevialle and Suffet 1987
monochloramine	swimming pool	0.65	Krasner et al. 1984
naphthalene*		0.0068	Mallevialle and Suffet 1987
nonanal	fragrant	0.001	Anselme et al. 1988
PAH's*			Mallevialle and Suffet 1987
phenol	phenol	1	Mallevialle and Suffet 1987
phenyl acetaldehyde	orange	0.004	Anselme et al. 1988
phthalates*			Anselme et al. 1985a
tetrachloroethylene*		0.03	Mallevialle and Suffet 1987
tributyl phosphate*			Anselme et al. 1985a
trichloramine	geranium	0.02	Krasner et al. 1984
2,3,6-trichloroanisole		3E-10	Mallevialle and Suffet 1987
2,4,6-trichloroanisole		0.00000003	Mallevialle and Suffet 1987
trichloroethylene*		0.48	Mallevialle and Suffet 1987
2,2,4-trimethyl pentane*			Anselme et al. 1985a

* indicates compound produced or extracted from materials used to contruct pipelines or water treatment plant

Appendix B - Tabulated Sniffing Data

Three different columns were used to determine if the retention times of the interesting odours in the samples matched those of known taste and odour causing chemicals. The results of these runs are tabulated in Table 5.13 and Table 5.14. Table 5.15 contains recovery data for selected organics that were spiked into organically pure water, passed over GAC and recovered by Soxhlet extraction.

Figures 5.1 to 5.7 are the graphical results of the sniffing experiments with the time being plotted against the intensity of the odours detected. The figures are arranged such that the extracts for the same solvent, on the same day, for each of the three streams, are shown on the same page. As an example, Figure 5.1 contains the plots of the hexane extracts from 4/5 April 1989 for the raw, treated with PAC and treated without PAC streams.

In all of the figures, the descriptive scale of weak, medium, strong and very strong were converted to a numerical scale to facilitate comparison and to reflect the logarithmic relationship between perceived intensity and concentration. The scale used was:

weak	1
medium	2
strong	4
very strong	8

Notes to Tables

1. Time indicates retention time on the column. Several odourgram runs are included in each Table and the times for all runs are in one column. Different runs are separated by a slash (/) for comparison purposes.

2. Asterisks (*) in time column indicate possible artifact as noted in solvent and carbon blanks.

3. Abbreviations used in Tables:

dd	defies description
W	weak intensity
M	medium intensity
S	strong intensity
V	very strong intensity
v	very
vint	very interesting
ETOAC	ethyl acetate
MEOH	methanol
ling	lingers
chem	chemical

Table B.1 Hexane and Carbon Extract Blanks
(see explanatory notes)

Retention Time (Solvent/Solvent & Carbon)	Solvent Blank	Solvent & Carbon Blank
3.48/3.32	solvent (W)	solvent (W)
6.51/----	hydrocarbon (W)	-
----/10.56	-	chemical (W)
----/12.45	-	vitamin C(S)
----/14.27	-	dd (VW)
----/14.51	-	chemical (M)
----/21.41	-	burnt (W)
----/27.18	-	dd (W)
----/32.12	-	chemical (W)
----/35.03	-	chemical (W)
----/35.28	-	chemical (W)
----/36.51	-	burny (W)

Table B.2 Dichloromethane and Carbon Extract Blanks
(see explanatory notes to tables)

Retention Time (Solvent/Solvent & Carbon)	Solvent Blank	Solvent & Carbon Blank
----/5.24	-	chemical (W)
7.13/----	chemical (W)	-
----/10.28	-	oil/chemical (W)
----/10.38	-	skunky (W)
11.09/----	light chemical (W)	-
----/12.30	-	vitamin C (M)
----/15.00	-	chemical (M)
----/15.44	-	hydrocarbon/skunky (VS)
----/18.45	-	chemical (W)
----/22.40	-	hydrocarbon (W)
----/23.05	-	hydrocarbon (W)
----/24.03	-	plastic (VW)
----/29.07	-	dd (W)
----/29.38	-	oil (S)
----/36.51	-	chemical (W)

Table B.3 Ethyl Acetate and Carbon Blanks
(see explanatory notes)

Retention Time (Solvent/Solvent & Carbon)	Solvent Blank	Solvent & Carbon Blank
3.50/3.58	ETOAC solvent (M)	ETOAC solvent (W)
—/4.31	-	ETOAC solvent (M)
—/4.59	-	solvent light (M)
6.41/----	chemical (VW)	-
6.57/6.51	chemical (M)	chemical plastic (S)
7.10/----	aldehyde (W)	-
7.18/----	sweet (M)	-
---/7.49	-	dd (W)
8.07/7.55	sweet (W)	MeOH sweet (W)
9.12/----	plastic (W)	-
9.21/9.32	dd (W)	chemical (W)
10.17/10.15	ice cream (W)	MeOH sweet(W)
11.08/----	chemical (W)	-
11.35/----	aldehyde sweatsocks (S)	-
12.00/----	dd (W)	-
12.42/12.47	dd (W)	vitamin C (M)
13.01/----	dd (W)	-
13.39/----	hydrocarbon (W)	-
---/14.08	-	aldehydic (M)
---/15.50	-	hydrocarbon (S)
15.56/----	hydrocarbon (W)	-
---/17.14	-	chemical (W)
17.55/----	dd (W)	-
---/19.37	-	chemical (M)
20.35/----	dd (W)	-
---/20.44	-	oil (S)
---/24.53	-	chemical (W)
---/35.36	-	chemical (W)

Table B.4 Sniffing Data for Hexane Extracts of 4/5 April 1989
(see explanatory notes to tables)

Retention Time (Raw/with PAC/ without PAC)	Raw	Treated with PAC	Treated without PAC
----/4.20/----	-	onion (W)	-
6.10/----/----	dd (W)	-	-
6.55/6.59/6.57*	plastic (M)	plastic (W)	chemical (M)
7.15/----/----	dd (W)	-	-
7.25/----/----	oil (M)	-	-
----/----/8.30	-	-	dd (W)
----/----/8.40	-	-	crude (M)
8.55/9.01/----	chemical (M)	heavy crude oil (W)	-
9.52/----/----	rotting (W)	-	-
10.15/----/----	rotting (W)	-	-
11.02/11.11/----	skunky (M)	skunky (W)	-
----/11.56/----	-	heavy crude oil (M)	-
12.10/----/----	sweatsocks (M)	-	-
12.32/12.34/12.35	sweatsocks (S)	skunky (W)	dd (W)
12.40/----/----	burning (W)	-	-
----/12.49/12.45*	-	vitamin C (M)	vitamin C (M)
12.50/12.56/12.50	hydrocarbon (S)	oil(VS)	crude (S)
13.05/----/----	chemical (M)	-	-
----/----/13.27	-	-	dd (W)
13.45/13.53/13.48	organic food (M)	stew	oily (M)
14.05/----/14.07	chemical (M)	-	plastic (W)
----/14.18/----	-	dd (W)	-
14.44/----/----	almonds (W)	-	-
14.57/----/----*	chemical (W)	-	-
----/15.08/15.04	-	chemical (M)	plastic heavier (M)
15.21/15.26/----	chemical (M)	oily (W)	-
----/15.47/----	-	stew (M)	-
15.58/16.03/15.56	chemical (S)	chemical (M)	marijuana (W)
16.26/----/----	marijuana (M)	-	-
16.40/----/----	marijuana (S)	-	-
----/17.00/16.57	-	plastic (W)	plastic (M)
17.05/----/----	plastic (W)	-	-
17.22/----/----	hydrocarbon (W)	-	-
17.30/17.29/----	plastic (M)	oily (M)	-
----/17.35/17.29	-	marijuana (M)	marijuana (M)
18.10/18.14/18.10	marijuana (S)	marijuana (S)	marijuana (W)
19.00/----/----	chemical (W)	-	-
20.25/----/----	chemical (W)	-	-
20.35/----/20.40	dd (M)	-	burning (M)
20.40/----/----	plastic (W)	-	-

Table B.4 (cont'd) Hexane Extracts from 4/5 April 1989
(see explanatory notes to tables)

Retention Time (Raw/with PAC/ without PAC)	Raw	Treated with PAC	Treated without PAC
21.22/----/21.20	dd (W)	-	plastic (W)
21.30/----/----	dd (M)	-	-
21.35/----/----	chemical(s)	-	-
----/----/22.02	-	-	plastic (W)
22.16/22.24/22.16	sour (M)	chemical (M)	sour (M)
----/22.40/22.29	-	chemical (M)	sour (M)
23.07/----/----	chemical (W)	-	-
23.12/----/----	sweatsocks (S)	-	-
23.52/----/----	dd (M)	-	-
24.04/24.08/----	rotting (W)	chemical (W)	-
24.13/----/----	chemical (W)	-	-
24.44/----/24.40	chemical (S)	-	-
24.55/25.00/----	chemical (S)	chemical (W)	-
26.00/26.03/----	orange (W)	chemical (M)	-
26.09/----/26.10	candy (W)	-	perfumy (W)
----/----/26.36	-	-	chemical (M)
26.57/----/----	dd (W)	-	-
26.57/----/26.51	chemical (W)	-	chemical ling (S)
27.10/----/----*	chemical (W)	-	-
29.40/----/----	plastic (W)	-	-
30.35/----/----	plastic (W)	-	-
31.28/----/31.28	dd (S)	-	earthy vint smell (S)
31.37/31.39/----	dd (S)	chemical (M)	-
----/32.10/----*	-	chemical (W)	-
32.35/----/----	dd (W)	-	-
34.45/----/----	dd (W)	-	-
36.18/----/----	chemical (W)	-	-
38.40/----/----	chemical (W)	-	-
40.26/----/----	pine (W)	-	-
----/40.41/----	-	spicy (W)	-
42.25/----/----	burning (W)	-	-
----/----/42.50	-	-	hydrocarbon (W)
46.05/----/----	chemical (W)	-	-
----/----/46.49	-	-	chemical

Table B.5 Sniffing Data for Ethyl Acetate Extracts of 4/5 April 1989
(see explanatory notes to tables)

Retention Time (Raw/with PAC/ without PAC)	Raw	Treated with PAC	Treated without PAC
3.15/----/3.18	sewer (M)	-	sewer (W)
4.35/----/----*	rotten (W)	-	-
----/5.20/----	-	ethyl acetate (W)	-
----/----/6.40*	-	-	aldehyde (W)
----/6.56/6.53*	-	dd (W)	rotting (W)
----/----/7.24	-	-	aldehyde (M)
----/----/7.55	-	-	dd(W)
9.20/----/9.27*	fruity (W)	-	plastic (M)
----/9.37/9.27	-	dd (W)	plastic (M)
10.20/10.40/10.35*	flowery (W)	flowers (W)	sweet like MeOH (W)
----/10.54/10.45	-	oily crude (M)	crude oil (M)
----/----/11.00	-	-	dd (W)
11.29/11.24/11.17*	foul (M)	skunky (S)	skunky (S)
11.50/11.43/11.49	dd (W)	dd (W)	chemical (M)
----/12.01/12.00	-	dd (W)	ice cream (W)
----/12.15/12.18	-	dd (W)	dd (W)
----/12.30/12.27	-	sour (M)	dd (W)
----/----/12.44*	-	-	offensive (M)
13.02/12.57/12.50	vitamin C (M)	vitamin C (M)	burnt almonds (S)
13.06/13.03/12.55	oil (S)	oily crude (S)	hydrocarbon oil(VS)
13.20/----/----	sweatsocks ling (S)	-	-
----/13.39/13.35	-	sweatsocks (W)	sweatsocks (M)
----/13.47/13.51	-	sweatsocks ling (S)	sweatsocks grossling(S)
13.59/----/----	offensive ling (S)	-	-
14.21/14.19/14.12*	offensive chemical (M)	chemical (S)	chemical (M)
----/14.30/14.16	-	vinegar (M)	vinegary (S)
14.48/14.49/14.41	burnt almonds (W)	burnt almonds sharp(S)	almonds (S)
15.03/----/14.51	solvent like (M)	-	dd (M)
15.14/----/15.07	chemical (S)	-	chemical (M)
----/----/15.38	-	-	chemical(W)
15.57/15.53/15.47*	crude oil (S)	chemical (S)	oil crude (S)
----/----/15.59	-	-	dd (S)
----/17.02/17.05	-	chemical (W)	organic gardeny (W)
17.27/----/----*	chemical (W)	-	-
17.32/----/17.30	sweatsocks (W)	-	sweat socks (W)
----/17.45/----	-	chemical (M)	-
----/18.47/----	-	almonds (W)	-
----/19.08/----	-	chemical (M)	-
19.14/19.08/19.07	chemical (M)	chemical (M)	chemical (W)
----/----/19.20	-	-	chemical (W)

Table B.5 (cont'd) Ethyl Acetate Extracts from 4/5 April 1989
(see explanatory notes to tables)

Retention Time (Raw/with PAC/ without PAC)	Raw	Treated with PAC	Treated without PAC
20.05/----/19.57	chemical (M)	-	chemical (W)
20.43/----/----	burnt (M)	-	-
21.06/21.08/20.51	bandaid (W)	chemical (M)	chemical plastic (M)
21.06/21.08/21.05	bandaid (W)	chemical (M)	chemical (M)
21.26/21.51/21.36	chemical (M)	chemical (W)	chemical (W)
22.00/----/21.59	sour (W)	-	chemical (S)
22.19/22.15/----	flowery (M)	chemical(W)	-
22.46/----/22.37	chemical (W)	-	dd (M)
22.57/----/----	sour (M)	-	-
23.15/23.05/23.02	plastic (S)	plastic chemical ling(M)	burning plastic ling (M)
23.46/----/23.40	wet canvas ling (M)	-	dd (W)
24.26/----/----	composty (M)	-	-
24.28/----/----	chemical (S)	-	-
----/----/24.40	-	-	plastic (M)
25.25/25.29/----	offensive (M)	chemical (W)	-
26.20/26.36/26.27	chemical (W)	sweet? (W)	black cat gum (W)
27.51/----/----	chemical (M)	-	-
28.05/28.10/----	chemical (M)	chemical (M)	-
----/2810/----	-	chemical (M)	-
29.01/----/----	dd (W)	-	-
29.22/----/----	rubber (M)	-	-
30.34/----/----	burnt (M)	-	-
31.06/----/----	chemical (M)	-	-
31.40/----/----	geranium (S)	-	-
31.57/----/----	dd (S)	-	-
----/----/32.05	-	-	dd (M)
33.33/----/33.10	dd (W)	-	chemical (W)
36.22/36.13/----	chemical (W)	chemical (W)	
----/39.36/----	-	chemical (W)	-
----/44.55/----	-	burnt (W)	-

Table B.6 Sniffing Data for Dichloromethane Extracts of 4/5 April 1989
(see explanatory notes to tables)

Retention Time (Raw/with PAC/ without PAC)	Raw	Treated with PAC	Treated without PAC
3.02/3.10/3.30	dd (W)	sewer (W)	dd (W)
4.20/----/----	solvent (W)	-	-
----/----/4.49	-	-	solvent (M)
5.37/----/----*	chemical (W)	-	-
----/6.05/----	-	dd (W)	-
6.54/6.54/----	dd (W)	chemical (M)	-
----/----/7.07	-	-	plastic (M)
----/7.18/----*	-	garlic? (W)	-
----/----/7.34	-	-	dd (W)
----/----/8.18	-	-	sweet like MeOH (W)
----/9.12/9.21	-	dd (W)	chemical (M)
----/----/10.02	-	-	dd (W)
10.38/----/----	ice cream (W)	-	-
10.45/----/----*	skunky (M)	-	-
----/11.06/11.12*	-	skunky (M)	skunky (S)
11.20/11.30/11.35	aldehydes (W)	aldehydes (M)	aldehydes (S)
----/11.39/11.45	-	oil crude (W)	crude oil (S)
----/12.24/12.22	-	dd (M)	chemical (W)
12.37/12.33/12.45*	oil crude (S)	sweat socks (S)	sweat socks (M)
----/12.44/12.50	-	almonds (S)	vitamin C (S)
12.52/12.52/12.55	sweat socks (M)	hydrocarbon oil (S)	crude oil ling (VS)
13.13/----/----	sweat socks (M)	-	-
----/----/13.21	-	-	skunky (M)
----/----/13.30	-	-	sweat socks (W)
13.45/13.47/----	dd (W)	dd (W)	-
14.10/14.08/14.13	almonds (M)	plastic ling (M)	dd (M)
14.42/----/14.48	dd (W)	-	crude (M)
15.00/----/----	chemical (M)	-	-
15.22/15.20/----*	oil (M)	crude oil (S)	-
----/----/15.47*	-	-	dd (M)
15.50/15.55/15.58	chemical (M)	odd/dd (S)	chemical ling to 1610(S)
16.06/16.11/----	skunky (M)	skunky (M)	-
----/----/16.47	-	-	dd (W)
16.55/16.57/16.58	plastic chemical (M)	plastic chemical (M)	chemical plastic (M)
17.10/17.15/17.12	chemical (M)	chemical (M)	organic (S)
17.30/17.32/17.32	chemical (M)	chemical interesting(M)	plastic (M)
18.08/----/----	chemical (W)	-	-
18.31/----/----	burnt (M)	-	-
----/----/18.51	-	-	dd (W)
----/----/19.08	-	-	chemical (W)

Table B.6 (cont'd) Dichloromethane Extracts from 4/5 April 1989
(see explanatory notes to tables)

Retention Time (Raw/with PAC/ without PAC)	Raw	Treated with PAC	Treated without PAC
19.58/----/----	plastic (W)	-	-
----/----/20.25	-	-	almonds (W)
20.49/----/----	chemical (W)	-	-
21.03/----/----	naphthalene (M)	-	-
----/21.16/----	-	potato bin! (W)	-
21.37/----/----	chemical (W)	-	-
22.41/22.20/----*	chemical (W)	chemical (W)	-
----/22.31/22.52	-	chemical (W)	dd (W)
23.08/23.06/23.07*	dd (W)	plastic (W)	plastic (W)
24.40/----/24.42	chemical (W)	-	chemical (M)
26.20/26.10/26.06	Black cat gum (W)	Black cat gum (W)	Black cat gum sweet(M)
----/----/29.13*	-	-	chemical (M)
30.08/30.02/30.03*	oil (W)	crude oil refinery (S)	crude oil(S)
----/30.34/----	-	chemical (W)	-
31.34/31.40/----	organic (M)	chemical burnt (W)	-
----/33.34/----	-	chemical like (S)	-
----/36.12/----	-	burnt paper (W)	-
----/41.14/----	-	garden (W)	-
----/42.38/----	-	chemical (W)	-
----/----/45.10	-	-	chemical (W)
----/46.08/----	-	chemical (W)	-
----/48.23/----	-	burnt smell (W)	-

Table B.7 Sniffing Data for Hexane Extracts of 5/6 April 1989
(see explanatory notes to tables)

Retention Time (Raw/with PAC/ without PAC)	Raw	Treated with PAC	Treated without PAC
----/----3.23	-	-	burnt (M)
----/----/3.59	-	-	burnt (M)
----/4.30/----	-	burning smell (M)	-
----/5.37/----	-	burning smell (M)	-
5.56/----/----	solvent (M)	-	-
----/6.39/----	-	burning smell (M)	-
7.07/----/----	solvent (W)	-	-
8.55/----/8.56	sweet like MeOH (W)	-	sweet like MeOH (M)
9.06/----/----	aldehydes (W)	-	-
----/----/9.48	-	-	chemical (W)
----/----/10.22	-	-	garden (M)
----/----/10.33	-	-	chemical (M)
----/----/10.47	-	-	chemical (W)
----/----/11.04	-	-	skunk (M)
----/11.37/11.36	-	chemical (W)	oil (W)
----/12.00/----	-	dd (M)	-
12.21/----/12.21	sweet like MeOH (M)	-	sweet (M)
12.37/12.38/12.37	dd (M)	dd (W)	chemical (S)
12.46/12.47/12.48*	hydrocarbon (S)	hydrocarbon smell (S)	hydrocarbon (S)
13.40/13.42/13.42	dd (M)	dd heavy (M)	organic stew (M)
14.04/14.05/14.05	chemical (S)	chemical (M)	plastic (M)
14.36/----/14.31	skunky (W)	-	skunk (W)
----/----/14.50	-	-	skunk (M)
15.01/15.01/----	dd (S)	chemical (W)	-
15.37/----/15.37	heavy smell (M)	-	chemical (M)
16.29/----/----	spicy (S)	-	-
----/----/16.56	-	-	plastic (W)
17.05/----/17.04	chemical (W)	-	chemical dd (M)
19.56/----/19.52	chemical (S)	-	kind of spicy (S)
----/----/20.48	-	-	chemical (M)
21.24/----/21.24	potato bin! (S)	-	chemical garden (S)
----/----/22.25	-	-	dd (W)
23.03/----/23.00	plastic chemical (M)	-	plastic (M)
23.27/----/23.25	dd (W)	-	plasticine (M)
23.47/----/----	odd (S)	-	-
----/----/24.07	-	-	dd (W)
24.20/----/----	chemical (W)	-	-
24.33/----/24.30	menthol camphor (S)	-	menthol camphor (S)
----/----/24.50	-	-	plastic (W)
----/----/25.54	-	-	sweet black cat gum(M)

Table B.7 (cont'd) Hexane Extracts from 5/6 April 1989
(see explanatory notes to tables)

Retention Time (Raw/with PAC/ without PAC)	Raw	Treated with PAC	Treated without PAC
26.37/----/26.41	bandaid (M)	-	chemical (W)
----/26.50/----	-	chemical (W)	-
27.04/27.01/27.12*	chemical (M)	chemical (W)	chemical (M)
----/----/27.39	-	-	chemical (M)
28.54/----/28.51	chemical (M)	-	dd (W)
----/----/29.56	-	-	dd (W)
30.09/30.18/30.18	chemical (S)	chemical (W)	plasticine (W)
30.22/30.18/30.18	chemical (M)	chemical (W)	plasticine (W)
31.07/31.10/31.14	dd (W)	chemical (W)	chemical (M)
31.18/31.22/31.21	musty ling vint (S)	sort of swampy (M)	vint ling light smell(S)
----/----/34.00	-	-	dd (M)
34.21/----/----	dd (M)	-	-
34.41/----/----	dd (W)	-	-
----/----/35.54	-	-	pepper (M)
----/37.21/----	-	chemical (W)	-
39.09/----/----	heavy chemical (M)	-	-
39.19/39.22/----	heavy chemical (M)	spicy ling (S)	-
----/----/44.17	-	-	chemical (W)
----/45.24/----	-	burning smell (W)	-
48.17/----/----	chemical (M))	-	-
48.37/----/----	chemical (M)	-	-

Table B.8 Sniffing Data for Ethyl Acetate Extracts of 5/6 April 1989
(see explanatory notes to tables)

Retention Time (Raw/with PAC/ without PAC)	Raw	Treated with PAC	Treated without PAC
3.47/----/----*	dd (M)	-	-
4.06/----/-----	dd (W)	-	-
----/4.42/4.38*	-	solvent (M)	solvent (M)
----/5.03/----*	-	solvent (W)	-
5.33/5.36/5.50	solvent (M)	solvent (W)	solvent (W)
6.02/----/----	solvent (S)	-	-
----/----/6.28	-	-	solvent (M)
6.27/6.51/6.46	aldehyde ling (M)	aldehyde (W)	aldehyde (S)
6.59/----/----	vinegary (M)	-	-
7.28/----/----*	aldehyde (M)	-	-
----/7.52/7.44*	-	dd (M)	dd (M)
8.20/----/----*	dd (W)	-	-
9.17/----/----*	dd (W)	-	-
9.30/9.11/9.09*	sweet like MeOH (M)	sweet like MeOH (M)	sweet like MeOH (M)
----/----/9.26	-	-	plastic (W)
----/9.35/9.39	-	aldehyde like (S)	dd (S)
9.44/----/----	plastic (S)	-	-
10.20/----/----	plastic (W)	-	-
10.50/10.41/10.47	aldehydes (W)	dd (M)	dd (W)
----/----/11.07*	-	-	sour (M)
11.13/----/----	sweat socks (W)	-	-
11.24/----/11.15	skunky (M)	-	skunk (S)
11.33/11.40/----*	sour ling (M)	sour (M)	-
----/----/11.47	-	-	chemical (M)
12.36/12.36/12.32	dd (S)	dd (S)	hydrocarbon (S)
12.44/12.49/12.47*	burning (S)	dd (S)	heavy (S)
12.58/12.57/12.57*	hydrocarbon (S)	hydrocarbon (S)	hydrocarbon (S)
13.15/13.06/13.08	sweatsocks & burning(S)	sweatsocks ling (S)	sweatsocks ling (S)
13.29/13.32/1325	sweatsocks (S)	sweatsocks ling (S)	sweatsocks ling (S)
13.38/13.59/1349	sweatsocks (S)	sweatsocks ling (S)	heavy (S)
14.16/14.07/13.59	almonds (S)	almonds (S)	almonds (S)
----/14.12/14.08	-	plastic (S)	hydrocarbon (S)
----/14.20/----	-	dd (S)	-
14.29/14.31/14.27	dd (S)	sour (S)	sour (S)
14.45/14.38/14.44	dd (S)	almond & sour (S)	almonds (M)
----/15.05/15.05	-	chemical (M)	dd (W)
15.40/15.44/15.41	dd (W)	chemical (S)	forest pine (S)
15.51/----/15.56	pine cone (S)	-	chemical (S)
----/16.02/----	-	stew (M)	-
16.23/16.17/16.16	earthy (S)	pine (M)	dd (M)

Table B.8 (cont'd) Ethyl Acetate Extracts from 5/6 April 1989
(see explanatory notes to tables)

Retention Time (Raw/with PAC/ without PAC)	Raw	Treated with PAC	Treated without PAC
16.48/16.44/16.45	sweet like MeOH (M)	sweet like MeOH (S)	sweet like MeOH (S)
----/----/16.53	-	-	chemical (S)
----/17.03/----	-	chemical (M)	-
17.11/----/----	mushrooms (W)	-	-
17.18/----/----	dd (M)	-	-
17.40/17.37/17.33	chemical (M)	chemical/plastic (S)	plastic/chemical (S)
17.48/----/----	chemical (M)	-	-
----/----/19.05	-	-	dd (M)
19.07/19.03/19.09	chemical (S)	chemical/plastic (S)	chemical (S)
19.16/19.22/----	dd (M)	heavy chemical (S)	-
19.39/19.38/19.34	almonds (S)	almond? (M)	heavy stew (M)
20.00/----/----	chemical ling (S)	-	-
20.16/----/----	coffee (M)	-	-
20.48/20.46/20.48*	dd (S)	chemical (M)	chemical (M)
20.55/20.51/----	chemical (S)	pesticide/fertilizer(M	-
----/21.08/----	-	dd (M)	-
----/----/21.19	-	-	chemical (S)
21.30/21.33/----	dd chemical (M)	chemical ling (S)	-
21.38/----/----	chemical (S)	-	-
----/21.55/----	-	chemical ling (S)	-
22.04/----/----	sour urine (S)	-	-
22.18/----/----	chemical (S)	-	-
22.27/22.24/22.27	dd (M)	urine sour (S)	chemical (M)
22.40/22.34/----	sweet (M)	pine forest ling (S)	-
----/----/22.54	-	-	dd (M)
23.35/23.26/----	chemical (M)	chemical (S)	-
23.59/23.54/23.51	chemical (S)	chemical (S)	chemical (M)
24.37/24.36/24.35	camphor/menthol (S)	menthol/camphor/pin ey (S)	menthol/piney (S)
----/----/24.50*	-	-	chemical (S)
----/----/25.26	-	-	dd (W)
26.05/26.04/25.57	black cat gum (S)	disinfectant (S)	black cat gum (S)
----/26.19/----	-	black cat gum (S)	-
26.48/----/26.47	chemical (M)	-	dd (M)
27.57/----/----	chemical (S)	-	-
----/----/28.22	-	-	chemical/plastic (M)
----/28.38/28.37	-	chemical (M)	chemical (M)
----/28.53/28.50	-	dd (W)	dd (W)
----/----/29.09	-	-	almonds (M)
----/29.31/29.39	-	chemical (W)	chemical (M)
30.18/----/30.05	plasticine (W)	-	plasticine (M)

Table B.8 (cont'd) Ethyl Acetate Extracts from 5/6 April 1989
(see explanatory notes to tables)

Retention Time (Raw/with PAC/ without PAC)	Raw	Treated with PAC	Treated without PAC
30.30/30.25/30.27	pine (M)	chemical (S)	forest (M)
----/----/30.40	-	-	pencils (S)
----/----/30.51	-	-	dd (M)
31.19/31.16/31.18	chemical (S)	forest rotting (S)	pine forest (S)
----/32.50/32.45	-	dd (W)	heavy (S)
33.15/----/33.30	dd (W)	-	dd (M)
----/34.04/----	-	dd (W)	-
----/----/35.20*	-	-	hydrocarbon (M)
----/37.23/----	-	chemical(W)	-
----/41.48/----	-	dd (M)	-
----/----/49.26	-	-	dd (M)

Table B.9 Sniffing Data for Dichloromethane Extracts of 5/6 April 1989
(see explanatory notes to tables)

Retention Time (Raw/with PAC/ without PAC)	Raw	Treated with PAC	Treated without PAC
----/----/3.23	-	-	burnt (W)
----/----/3.32	-	-	dd (M)
----/----/4.03	-	-	dd (M)
----/5.28/----*	-	solvent (W)	-
----/6.02/----	-	solvent ling (W)	-
----/----/7.42	-	-	burnt (M)
----/8.21/8.38	-	dd (M)	hydrocarbon (W)
----/9.10/----	-	sweet like MeOH (M)	-
9.41/----/----	almonds (W)	-	-
----/10.05/----	-	chemical(W)	-
----/12.34/----	-	sweatsocks (M)	-
12.40/12.42/12.40*	dd (M)	sweatsocks (M)	hydrocarbon (S)
----/12.55/12.50	-	hydrocarbon (S)	dd (W)
----/----/13.36	-	-	organic (M)
----/14.07/13.59	-	plastic chemical (S)	plastic chemical (M)
----/14.18/----	-	plastic chemical (M)	-
15.17/15.23/15.19	chemical (M)	dd (S)	coffee beans sharp (S)
15.41/15.46/15.38*	hydrocarbon (S)	aldehydes (S)	chemical (S)
16.05/16.06/16.01	skunk (S)	skunk (S)	skunky (S)
----/16.50/----	-	dd (M)	-
----/17.26/----	-	plastic/chemical ling(S)	-
----/----/17.40	-	-	chemical (W)
18.03/----/----	chemical (M)	-	-
----/19.02/----	-	plastic/chemical (W)	-
----/20.55/----	-	chemical (M)	-
----/21.07/21.07	-	chemical ling (W)	chemical (W)
----/21.18/21.17	-	chemical (M)	chemical (W)
22.07/22.09/----	sour (M)	dd (W)	-
----/22.20/22.13	-	chemical (M)	sample smell (S)
----/23.22/----	-	chemical (M)	-
----/24.02/----*	-	naphthalene (W)	-
----/24.13/----	-	black cat gum (M)	-
26.01/25.55/25.59	black cat gum (M)	chemical ling (M)	sweet black cat gum ling(M)
26.37/----/----	bandaid (M)	-	-
----/26.45/----	-	chemical ling (M)	-
----/----/27.30	-	-	dd (W)
27.45/----/----	dd (W)	-	-
28.09/----/----	sewer (W)	-	-
----/28.49/----	-	dd (W)	-
----/----/29.12*	-	-	chemical (W)

Table B.9 (cont'd) Dichloromethane Extracts from 5/6 April 1989
(see explanatory notes to tables)

Retention Time (Raw/with PAC/ without PAC)	Raw	Treated with PAC	Treated without PAC
----/----/29.46*	-	-	dd (M)
29.55/29.52/29.51	dd (M)	aldehyde like (M)	heavy chemical (S)
30.10/----/30.10	plastic chemical (M)	-	sweet not MeOH (M)
----/30.26/----	-	dd (M)	-
30.54/----/----	burnt (W)	-	-
31.19/----/----	foresty (S)	-	-
31.52/----/----	dd (W)	-	-
----/33.13/----	-	skunk (W)	-
34.01/----/34.01	dd (W)	-	plasticine (W)
----/35.25/----	-	kind of oily (W)	-
35.42/----/----	dd (W)	-	-
----/37.05/----*	-	dd (W)	-
----/37.33/----	-	almond (W)	-
38.43/----/----	heavy (W)	-	-
----/----/39.14	-	-	dd (S)
----/----/39.31	-	-	almondy (S)
----/----/40.44	-	-	dd (W)
----/----/43.17	-	-	stewlike (M)
----/----/45.50	-	-	almonds (M)
----/46.23/----	-	burning heavy (M)	-
----/46.40/----	-	stewlike (M)	-

Table B.10 Sniffing Data for Hexane Extracts of 6/7 April 1989
(see explanatory notes to tables)

Retention Time (Raw/with PAC/ without PAC)	Raw	Treated with PAC	Treated without PAC
3.27/----/----*	solvent (M)	-	-
----/----/4.55	-	-	solvent (W)
----/5.08/----	-	solvent (W)	-
----/----/5.44	-	-	solvent (W)
----/----/6.29	-	-	almonds (W)
----/7.14/----	-	chemical (W)	-
----/8.54/8.52	-	fruity (W)	sweet like MeOH (W)
----/9.12/9.07	-	chemical (M)	aldehyde (M)
----/10.19/10.19	-	dd (M)	stale (M)
10.33/10.35/10.33	skunky (S)	hydrocarbon (M)	oil (M)
11.06/----/----	skunky (W)	-	-
----/11.26/11.28	-	aldehyde (M)	nauseous aldehyde (M)
11.38/----/11.38	dd (M)	-	oil (M)
----/----/12.22	-	-	sweet like MeOH (W)
----/12.38/12.36	-	dd (M)	burnt almonds (S)
12.48/12.46/12.47*	hydrocarbon heavy oil(S)	hydrocarbon (S)	hydrocarbon (S)
13.43/13.41/13.41	dd (S)	dd (S)	dd (S)
----/----/13.58	-	-	dd (M)
14.06/14.06/14.07	dd chemical (M)	plastic/chemical (M)	plastic (M)
14.47/14.35/----*	skunky (M)	skunky (M)	-
15.00/14.58/14.59	dd (W)	skunky (M)	oily (W)
----/----/15.08	-	-	dd (W)
----/----/16.40	-	-	dd (M)
----/17.07/17.06	-	rotting (W)	chemical (S)
----/18.25/----	-	almonds (M)	-
----/----/19.03	-	-	chemical (W)
----/19.49/19.52	-	dd (W)	spicy (M)
20.45/20.46/20.44	oily (M)	chemical (M)	mushroom (W)
----/----/20.50	-	-	plastic (M)
----/21.25/21.25	-	garden/vegetable (S)	geranium like (S)
----/----/22.17	-	-	dd (W)
----/22.58/22.58	-	plastic (M)	plastic/chemical (S)
----/----/23.19	-	-	chemical (M)
23.47/----/----	chemical (M)	-	-
24.03/24.07/24.05	dd (S)	potato (W)	gardeny (W)
24.29/24.29/24.29	camphor menthol vint (S)	camphor menthol (S)	camphor menthol (S)
----/24.43/24.47	-	dd (S)	oil (W)
26.05/----/26.04	dd (W)	-	black cat gum (W)
26.33/----/----	dd (W)	-	-
26.43/26.36/----	chemical (S)	dd (W)	-

Table B.10 (cont'd) Hexane Extracts from 6/7 April 1989
(see explanatory notes to tables)

Retention Time (Raw/with PAC/ without PAC)	Raw	Treated with PAC	Treated without PAC
27.00/27.02/27.01	chemical (M)	dd (M)	chemical (M)
----/----/27.40	-	-	dd (W)
----/28.24/28.19	-	hydrocarbon (M)	chemical (W)
28.53/28.56/28.57	dd (W)	dd (M)	dd (M)
29.11/----/----	chemical (W)	-	-
----/----/29.57	-	-	plastic (W)
30.09/----/----	dd (W)	-	-
30.14/----/----	dd (M)	-	-
----/30.24/----	-	plastic (W)	-
31.14/31.12/----	woodsy ling (W)	dd (M)	-
31.19/31.25/31.17	woodsy ling (S)	dd (S)	musty sample ling (S)
34.01/----/34.03	chemical (M)	-	chemical (W)
34.25/----/----	chemical (M)	-	-
----/----/38.23	-	-	rotting (S)
----/----/38.41	-	-	rotting (S)
39.07/39.05/38.59	pepper (W)	pepper (M)	burning (S)
----/----/39.19	-	-	dd (S)
----/40.10/----	-	hydrocarbon (W)	-
40.27/----/----	rotting (W)	-	-
40.51/----/----	chemical (M)	-	-
----/----/41.57	-	-	burning (S)

Table B.11 Reproducibility of Sniffing Data
Treated Water with no PAC from 4/6 April 1989
(see explanatory notes to tables)

Retention Time (Sniffer #1/ Sniffer #2)	Sniffer #1 (D. Rector)	Sniffer #2 (N. Best)
1.48/1.48	sewer (W)	sewage (M)
1.54/----	solvent (M)	-
1.59/----	rotting garden (M)	-
----/2.09	-	dd (W)
2.17/2.19	dd (W)	natural gas (M)
3.23/----	dd (W)	-
3.36/----	chemical (M)	-
3.52/3.59*	chemical (M)	oil (M)
4.00/----	hydrocarbon (M)	-
4.42/----*	dd (M)	-
5.25/5.22	hydrocarbon (S)	oil (W)
5.49/----	dd (W)	-
5.56/5.54	hydrocarbon (M)	oil (W)
6.40/----	vitamin C (W)	-
----/7.56*	-	dd (W)
8.05/----*	dd (W)	-
8.14/8.09	heavy hydrocarbon (S)	gas (S)
8.20/----	heavy hydrocarbon (S)	-
----/8.40	-	chemical (M)
9.34/----	garden (M)	-
10.12/10.14	skunky (M)	skunk (M)
11.01/----	dd(chemical) (S)	-
11.28/11.29*	dd(chemical) (S)	chemical (W)
12.18/12.17	chemical (S)	garlic (M)
12.41/----*	spicy (M)	-
13.24/13.25	dd (W)	dd (W)
13.40/----*	chemical (M)	-
13.57/13.58	hydrocarbon (M)	oil (W)
14.20/14.18	hydrocarbon (M)	dd (W)
15.48/----	chemical (W)	-
16.39/----	hydrocarbon (S)	-
----/16.46	-	garlic (W)
16.55/16.57	hydrocarbon (S)	dd (W)
17.31/17.31	dd (M)	dd (M)
17.48/17.48	spicy (S)	dd (W)
18.13/----	socks? (S)	-
18.35/18.35	dd (M)	old rubber (M)
19.09/----	chemical (M)	-
19.20/19.20	dd (M)	onion (M)
19.30/----*	odd (S)	-
19.50/----	dd (M)	-
20.06/20.06	gardeny (M)	dd (W)

Table B.11 (cont'd) Reproducibility of Sniffing Data
(see explanatory notes to tables)

Retention Time (Sniffer #1/ Sniffer #2)	Sniffer #1 (D. Rector)	Sniffer #2 (N. Best)
20.47/20.46	garden (S)	plants/grass (M)
20.55/----	chives (M)	-
21.26/----	dd (M)	-
22.09/----	dd (W)	-
22.13/----	dd (W)	-
22.44/22.44	garden like (W)	dd (W)
22.59/----	plastic (S)	-
23.24/23.27	spicy (M)	plants (M)
23.47/23.49	plasticine (S)	plastic (W)
24.52/24.54	forest (M)	oil (W)
----/25.10	-	flowery (W)
25.17/25.19	camphor/menthol (S)	camphor (S)
27.05/----	sour (M)	-
27.20/----	plastic (M)	-
28.05/----	dd (W)	-
28.23/28.24	black cat gum (W)	black cat gum (M)
29.30/----	chemical fertilizer (S)	-
30.31/30.31	old (M)	soil(greenhouse) (M)
----/30.50	-	sweet tobacco (M)
31.04/31.09	earthy (S)	musty moldy (S)
----/32.14	-	dd (W)
32.54/----	chemical (W)	-
----/33.01	-	flowery (W)
34.08/----	garden (M)	-
34.57/----	dd (M)	-
35.28/----	sweet black cat gum (S)	-
36.35/----	peppery (W)	-
36.37/----	wet canvas (M)	-
----/36.53	-	dd (W)
37.01/37.00	chemical fertilizer (M)	plastic (W)
38.29/----	chemical (M)	-
----/38.40	-	pine (W)
38.57/----	celery!!! (M)	-
39.09/----	spicy (M)	-
39.21/----	chemical (M)	-
40.04/----	canvas (W)	-
40.37/40.52	spicy (M)	spicy? (W)
43.20/----	odd (W)	-
43.50/----	chemical (S)	-
45.32/----	odd (W)	-
45.44/----	chemical/flowery (S)	-

Table B.12 Treated Water Dichloromethane Extract (60 L) of 5 April 1989
(see explanatory notes to tables)

Acid Extract (analyzed 27 FEB 90)	
RT	Descriptor
4.06	concrete (M)
5.55	solvent (W)
8.55	aldehyde (M)
8.59	aldehyde (W)
10.43	sweat socks (S)
11.03	dd (M)
11.13	chemical (VS)
11.26	dd (M)
11.40	sour (S)
11.51	sour lingers (S)
12.35	different (S)
12.49	different (S)
13.01	oily (M)
13.09	sweatsocks lingers to 1330 (S)
13.48	dd (S)
14.37	almonds (M)
14.52	chemical (S)
15.23	forestry (S)
15.34	dd (M)
16.01	vanilla (M)
16.18	dd (M)
17.05	rotting (S)
17.32	plastic/chemical lingers (S)
18.01	dd (M)
18.30	almonds (W)
18.59	chemical (S)
19.09	flowery (M)
19.40	burnt almonds (VS)
19.50	sour (M)
20.00	dd (S)
20.08	chemically(sensationtoo)(VS)
20.28	chemical (S)
20.46	mushroom (S)
20.57	chemical/plastic (VS)
21.17	forest (S)
21.28	chemical lingered to 2142(VS)
21.50	almonds (S)
22.23	chemical (S)
23.05	plastic (S)
23.27	plasticine (S)

Acid Extract (analyzed 27 FEB 90)	
RT	Descriptor
23.59	chemical (S)
24.19	chemical (M)
24.35	chemical (M)
24.42	beer(stale) (M)
24.56	fertilizer (S)
25.10	chemical (M)
25.59	black cat gum (S)
26.10	sweet disinfectant (S)
26.22	plastic (S)
26.49	very interesting dd (S)
27.01	dd (M)
27.55	chemical (S)
28.54	dd (W)
28.58	crayon (M)
29.05	crayon lingers (S)
30.23	chemical (S)
30.39	dd (S)
31.18	piney forest (VS)
34.08	dd (M)
35.39	pepper (M)
42.50	almonds (W)
43.42	chemical (W)
47.06	burnt (W)

Solvent blank had one odour - chemical(w) at 5.59

Table B.13 Comparison of Sniffing Data for Carbon Extracts and Liquid-Liquid Extractions
(see explanatory notes to tables)

Retention Time (Raw/with PAC/ without PAC)	Raw	Treated with PAC	Treated without PAC	RT	60L Acid Extract
----/----3.23	-	-	burnt (M)	-	-
----/----/3.59	-	-	burnt (M)	4.06	concrete (M)
----/4.30/----	-	burning smell(M)	-	-	-
----/5.37/----	-	burning smell(M)	-	-	-
5.56/----/----	solvent (M)	-	-	5.55	solvent (W)
----/6.39/----	-	burning smell(M)	-	-	-
7.07/----/----	solvent (W)	-	-	-	-
8.55/----/8.56	sweet like MeOH (W)	-	sweet like MeOH (M)	8.55	aldehyde (M)
9.06/----/----	aldehydes (W)	-	-	8.59	aldehyde (W)
----/----/9.48	-	-	chemical (W)	-	-
----/----/10.22	-	-	garden (M)	-	-
----/----/10.33	-	-	chemical (M)	-	-
----/----/10.47	-	-	chemical (W)	10.43	sweatsocks (S)
----/----/11.04	-	-	skunk (M)	11.03	dd (M)
-	-	-	-	11.13	chemical (VS)
-	-	-	-	11.26	dd (M)
----/11.37/11.36	-	chemical (W)	oil (W)	11.40	sour (S)
----/12.00/----	-	dd (M)	-	11.51	sour lingers (S)
12.21/----/12.21	sweet like MeOH (M)	-	sweet (M)	-	-
12.37/12.38/12.37	dd (M)	dd (W)	chemical (S)	12.35	different (S)
12.46/12.47/12.48	hydrocarbon (S)	hydrocarbon smell (S)	hydrocarbon (S)	12.49	differentv
-	-	-	-	13.01	oily (S)
-	-	-	-	13.09	sweatsocks ling 13.30
13.40/13.42/13.42	dd (M)	dd heavy (M)	organic stew (M)	13.48	dd (S)
14.04/14.05/14.05	chemical (S)	chemical (M)	plastic (M)	-	-
14.36/----/14.31	skunky (W)	-	skunk (W)	14.37	almonds (M)
----/----/14.50	-	-	skunk (M)	14.52	chemical (S)
15.01/15.01/----	dd (S)	chemical (W)	-	-	-
-	-	-	-	15.23	foresty (S)
15.37/----/15.37	heavy smell (M)	-	chemical (M)	15.34	dd (M)
-	-	-	-	16.01	vanilla (M)
-	-	-	-	16.18	dd (M)
16.29/----/----	spicy (S)	-	-	-	-
----/----/16.56	-	-	plastic (W)	-	-
17.05/----/17.04	chemical (W)	-	chemical dd (M)	17.05	rotting (S)
-	-	-	-	17.32	plastic/chem ling (S)
-	-	-	-	18.01	dd (M)
-	-	-	-	18.30	almonds (W)

Table B.13 (cont'd) Comparison of Sniffing Data for Carbon Extracts and Liquid-Liquid Extractions (see explanatory notes to tables)

Retention Time (Raw/with PAC/ without PAC)	Raw	Treated with PAC	Treated without PAC	RT	60L Acid Extract
-	-	-	-	18.59	chemical (S)
-	-	-	-	19.09	flowery (M)
-	-	-	-	19.40	burnt almonds (VS)
-	-	-	-	19.50	sour (M)
19.56/----/19.52	chemical (S)	-	kind of spicy (S)	20.00	dd (S)
-	-	-	-	20.08	chem-sensation too (VS)
-	-	-	-	20.28	chemical (S)
----/----/20.48	-	-	chemical (M)	20.46	mushroom (S)
-	-	-	-	20.57	chemical/ plastic (VS)
-	-	-	-	21.17	forest (S)
21.24/----/21.24	potato bin! (S)	-	chemical garden (S)	21.28	chem ling to 21.42 (VS)
-	-	-	-	21.50	almonds (S)
----/----/22.25	-	-	dd (W)	22.23	chemical (S)
23.03/----/23.00	plastic chemical (M)	-	plastic (M)	23.05	plastic (S)
23.27/----/23.25	dd (W)	-	plasticine (M)	23.27	plasticine (S)
23.47/----/----	odd (S)	-	-	-	-
----/----/24.07	-	-	dd (W)	23.59	chemical (S)
24.20/----/----	chemical (W)	-	-	24.19	chemical (M)
24.33/----/24.30	menthol camphor (M)	-	menthol camphor (S)	24.35	chemical (M)
----/----/24.50	-	-	plastic (W)	24.42	beer-stale (M)
-	-	-	-	24.56	fertilizer (S)
-	-	-	-	25.10	chemical (M)
----/----/25.54	-	-	sweet black cat gum (M)	25.59	black cat gum (S)
-	-	-	-	26.10	sweet disinfectant (S)
-	-	-	-	26.22	plastic (S)
26.37/----/26.41	bandaid (M)	-	chemical (W)	-	-
----/26.50/----	-	chemical (W)	-	26.49	very interesting dd (S)
27.04/27.01/27.12	chemical (M)	chemical (W)	chemical (M)	27.01	dd (M)
----/----/27.39	-	-	chemical (M)	-	-
-	-	-	-	27.55	chemical (S)
28.54/----/28.51	chemical (M)	-	dd (W)	28.54	dd (W)

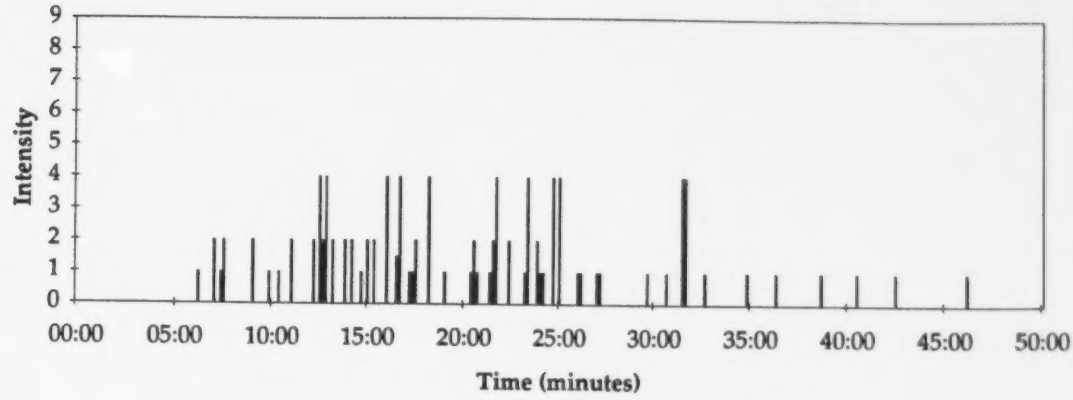
Table B.13 (Cont'd) Comparison of Sniffing Data for Carbon Extracts and Liquid-Liquid Extractions (see explanatory notes to tables)

Retention Time (Raw/with PAC/ without PAC)	Raw	Treated with PAC	Treated without PAC	RT	60 litre Acid Extract
-	-	-	-	28.58	crayon (M)
-	-	-	-	29.05	crayon ling (S)
----/----/29.56	-	-	dd (W)	-	-
30.09/30.18/30.18	chemical (S)	chemical (W)	plasticine (W)	-	-
30.22/30.18/30.18	chemical (M)	chemical (W)	plasticine (W)	30.23	chemical (S)
-	-	-	-	30.39	dd (S)
31.07/31.10/31.14	dd (W)	chemical (W)	chemical (M)	-	-
31.18/31.22/31.21	musty ling vint (S)	sort of swampy (M)	vint ling light smell (S)	31.18	piney forest (VS)
----/----/34.00	-	-	dd (M)	34.08	dd (M)
34.21/----/----	dd (M)	-	-	-	-
34.41/----/----	dd (W)	-	-	-	-
----/----/35.54	-	-	pepper (M)	35.39	pepper (M)
----/37.21/----	-	chemical (W)	-	-	-
39.09/----/----	heavy chemical (M)	-	-	-	-
39.19/39.22/----	heavy chemical (M)	spicy ling (S)	-	-	-
-	-	-	-	42.50	almonds (W)
-	-	-	-	43.42	chemical (W)
----/----/44.17	-	-	chemical (W)	-	-
----/45.24/----	-	burningsmell(W)	-	-	-
-	-	-	-	47.06	burnt (W)
48.17/----/----	chemical (M)	-	-	-	-
48.37/----/----	chemical (M)	-	-	-	-

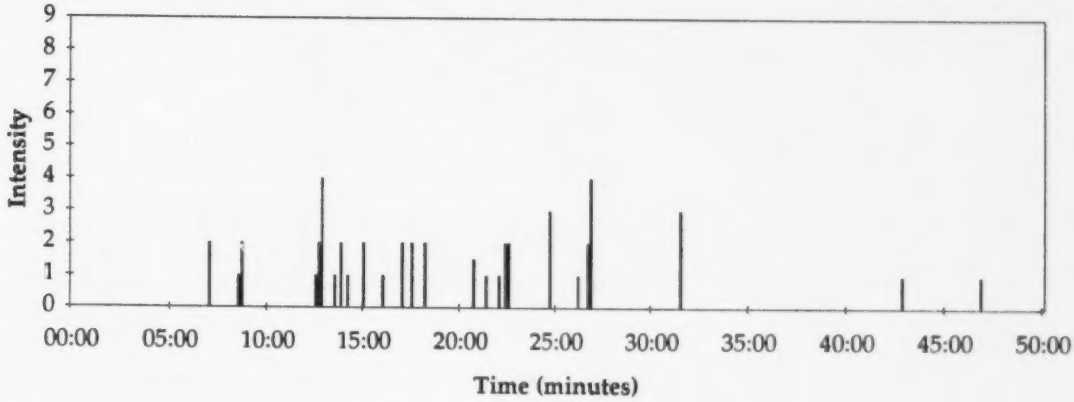
Appendix C - Gas Chromatography Sniffing Figures

Figure C.1 Odourgrams of the Hexane Extracts from 4/5 April 1989

Raw



Treated without PAC



Treated with PAC

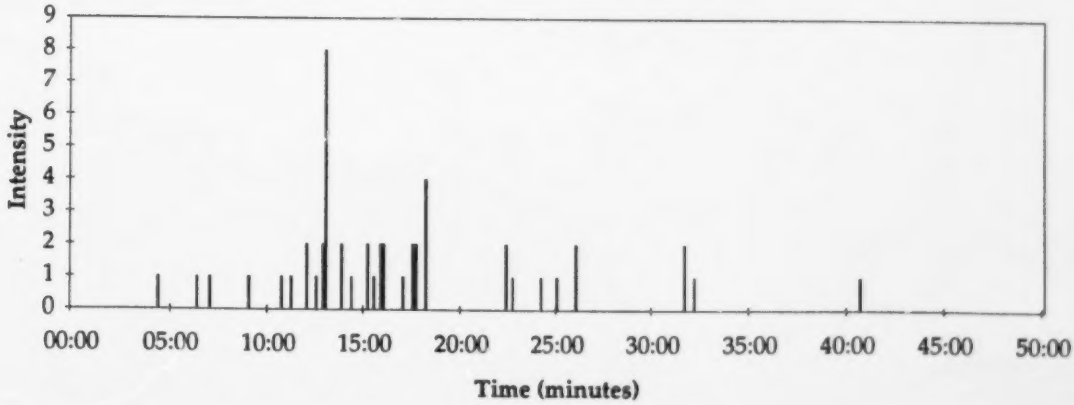
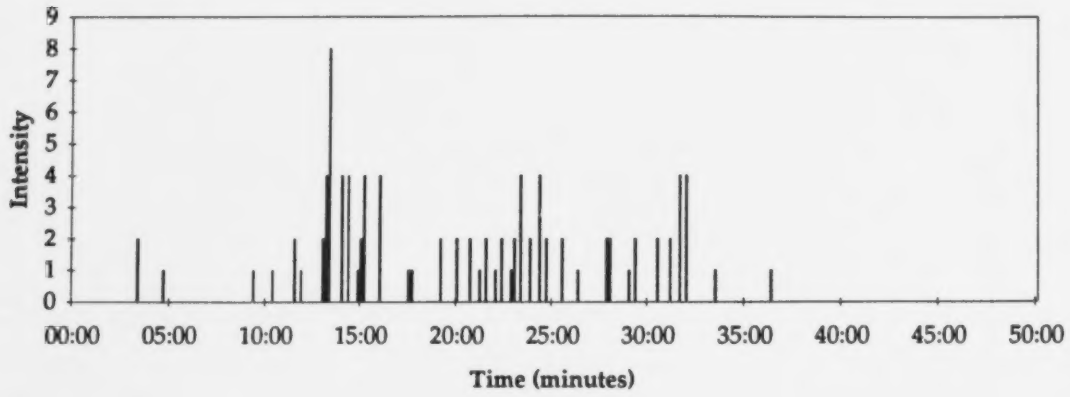
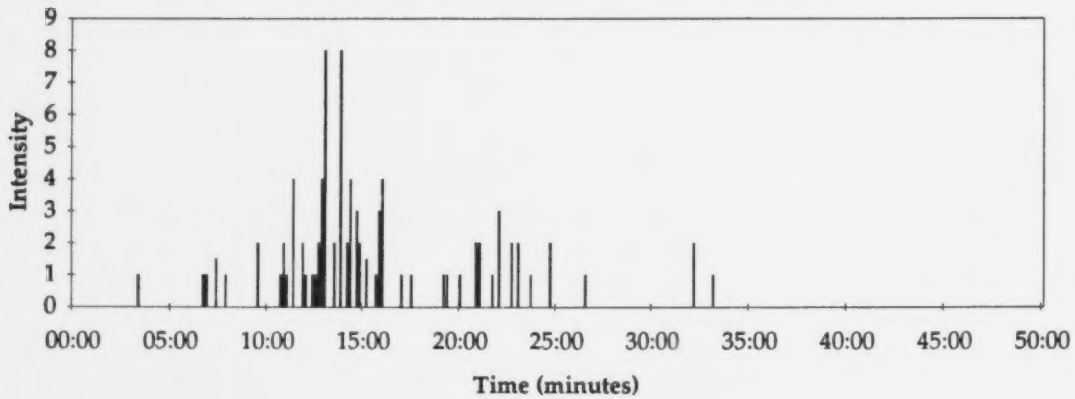


Figure C.2 Odourgrams of the Ethyl Acetate Extracts from 4/5 April 1989

Raw



Treated without PAC



Treated with PAC

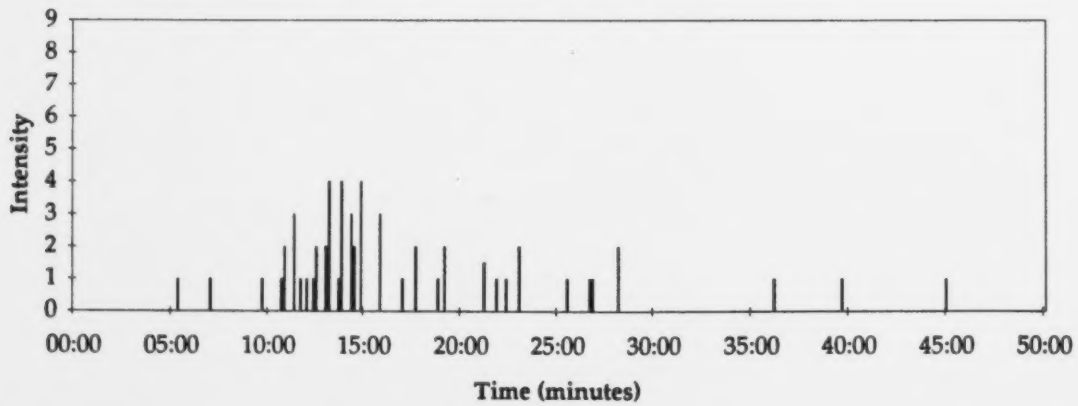
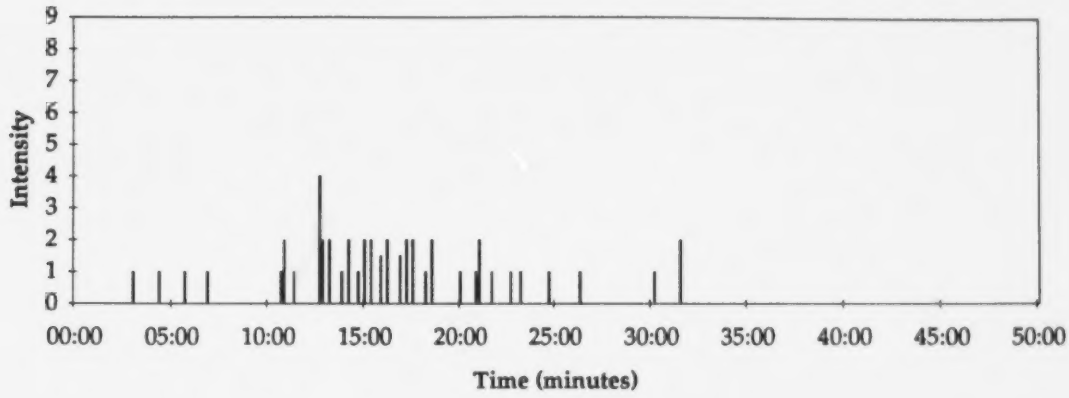
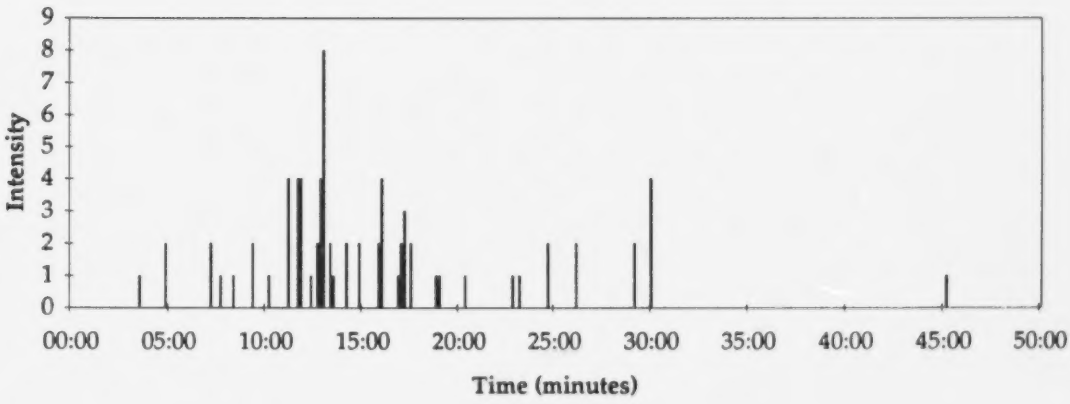


Figure C.3 Odourgrams of the Dichloromethane Extracts from 4/5 April 1989

Raw



Treated without PAC



Treated with PAC

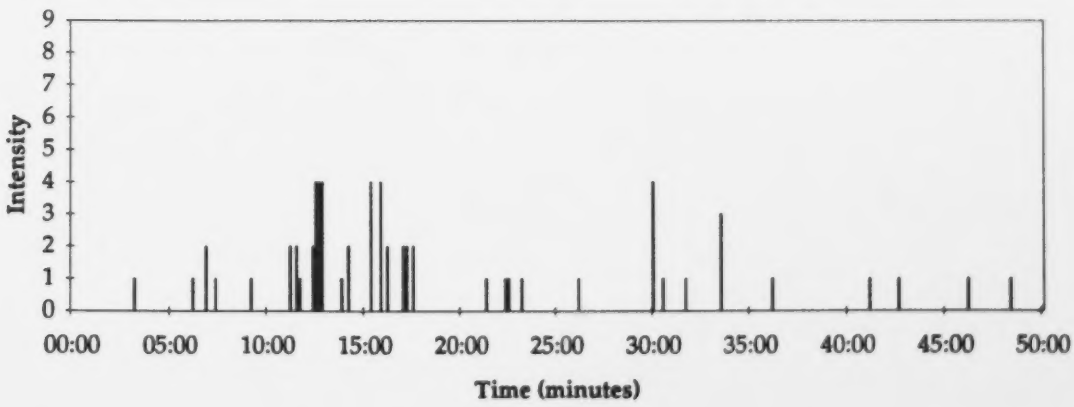
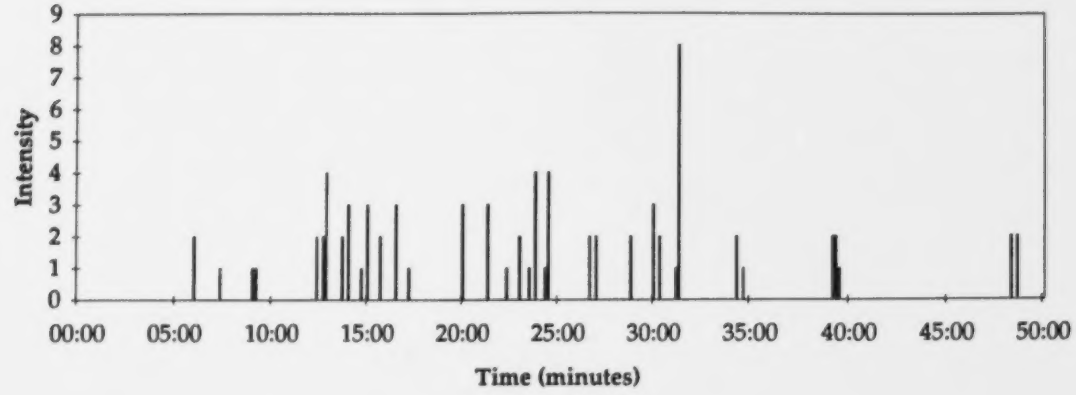
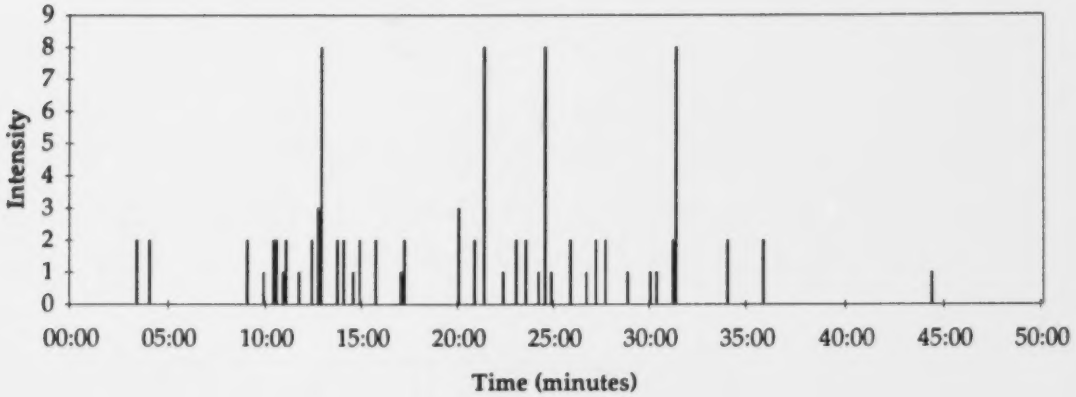


Figure C.4 Odourgrams of the Hexane Extracts from 5/6 April 1989

Raw



Treated without PAC



Treated with PAC

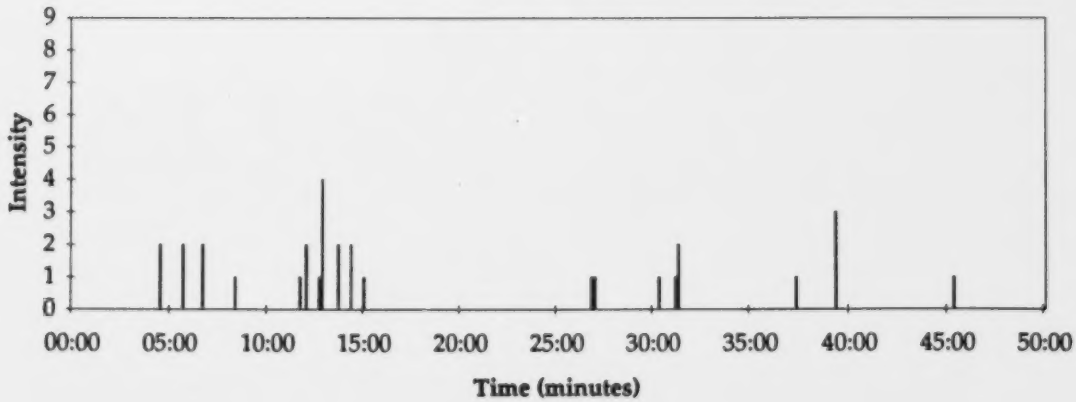
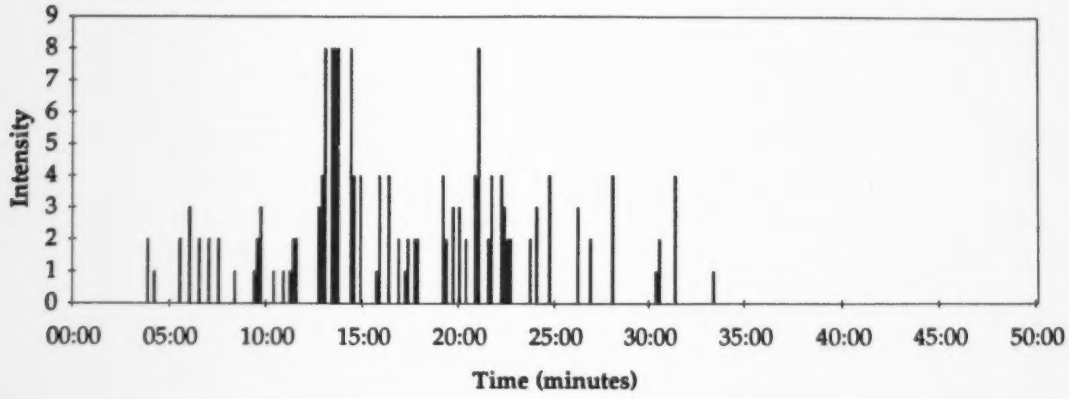
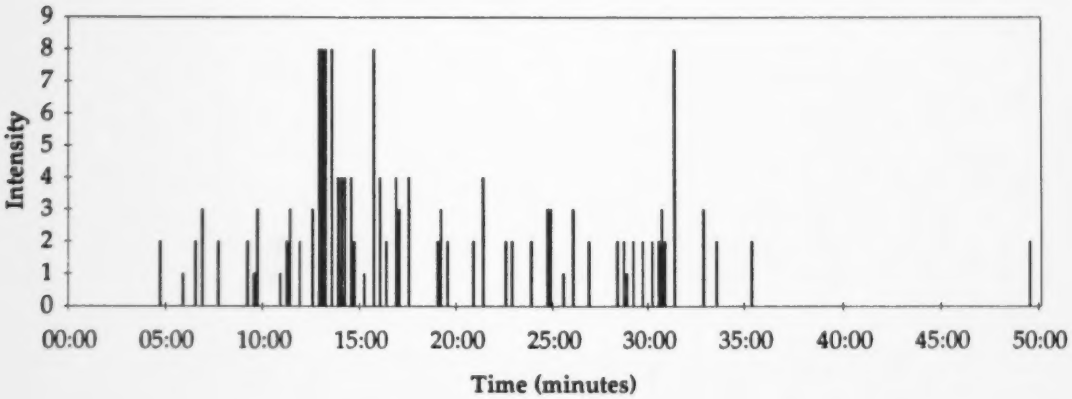


Figure C.5 Odourgrams of the Ethyl Acetate Extracts from 5/6 April 1989

Raw



Treated without PAC



Treated with PAC

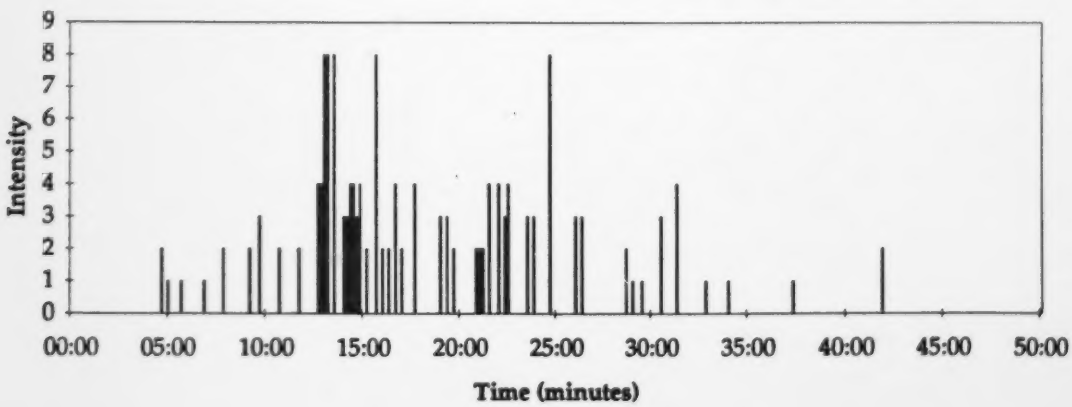
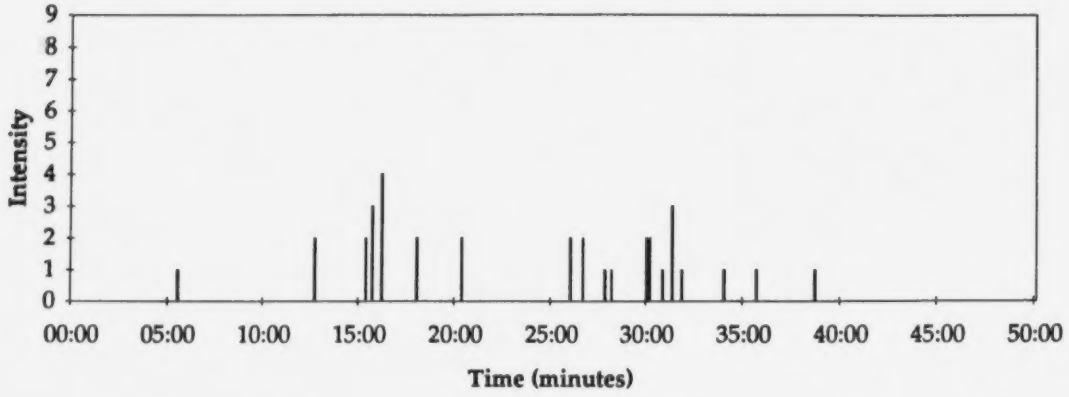
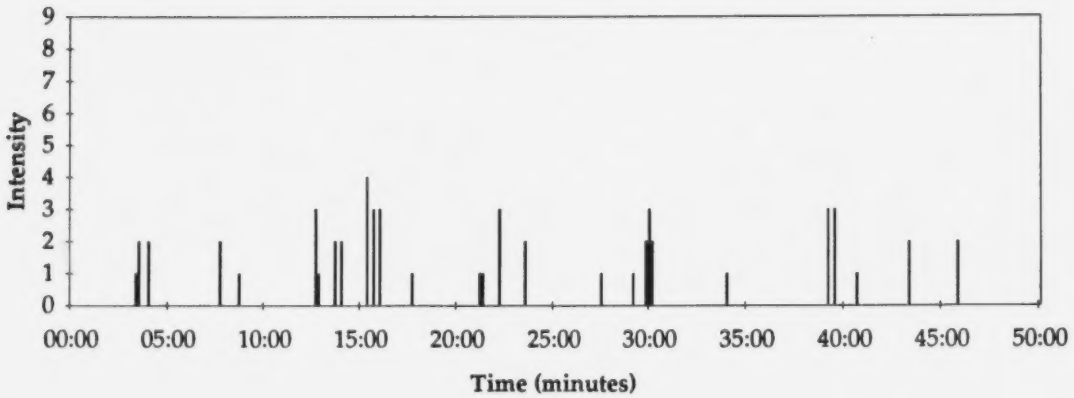


Figure C.6 Odourgrams of the Dichloromethane Extracts from 5/6 April 1989

Raw



Treated without PAC



Treated with PAC

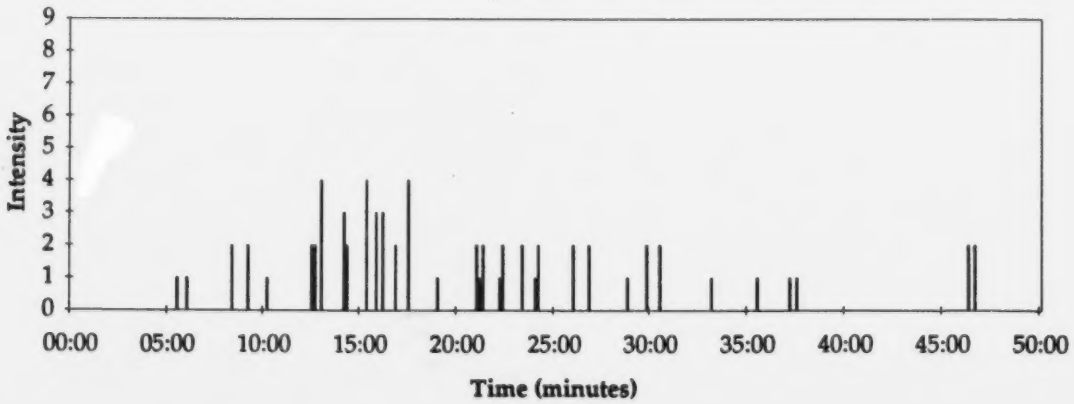
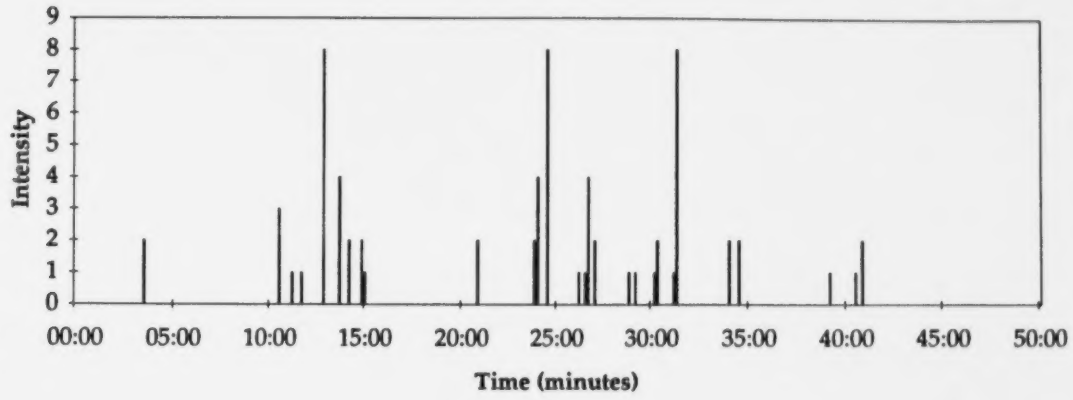
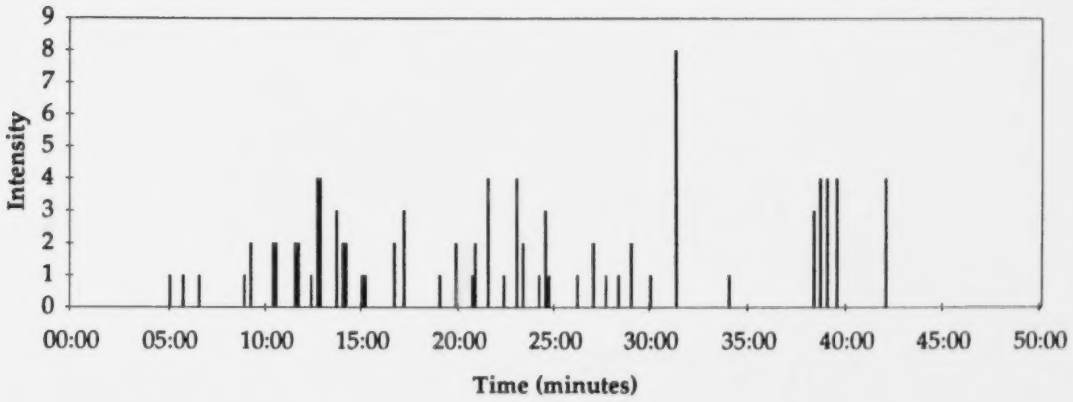


Figure C.7 Odourgrams of the Hexane Extracts from 6/7 April 1989

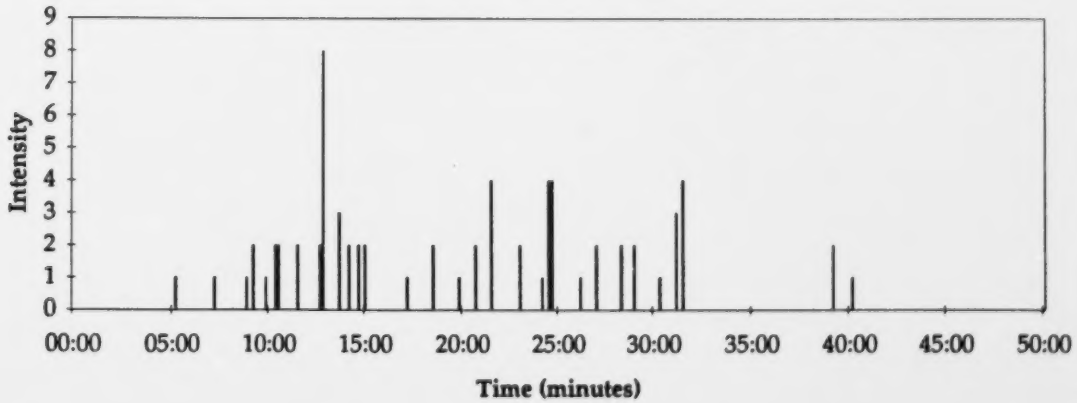
Raw



Treated without PAC



Treated with PAC



Appendix D - Preparative Gas Chromatography

Preparative Gas Chromatography Methodology

This work was based upon the work of Lundgren et al. (1988b) who used this technique to identify the odorous fractions of a drinking water extract in the Sweden. In this series of experiments, certain fractions of the chromatograms were frozen out for concentration and analysis. In order to accomplish this, two dewar flasks were constructed (Technical Services Glass Shop) to facilitate the introduction of tubes to collect the required fractions and for storage of the frozen tubes. Figure D.1 shows the various designs of the freezing out tubes and Figures D.2 and D.3 show the two designs used for the glass dewars.

For the initial design the FID and jet were removed and the capillary column pushed up similarly to the sniffing set up. A small piece of stainless steel tubing was placed over the column and a pathway formed up through the dewar with a glass tube. Teflon® tape was wrapped around the stainless steel tube until a seal was formed between it and the glass tube. A Vespel® ferrule was put on top of the column to center it and Teflon® tape was added to form a seal with the concentration tubes. As it was found to be very difficult to place the Teflon® tape over the column and on the ferrule, the ferrule was discarded and the Teflon® tape was wrapped around the top of the stainless steel tube and column which centered and formed the required seals.

Modifications to the above design were required as the recoveries obtained were unacceptably low or non-existent. It was postulated that the above design gave poor results as the effluent from the column was not reaching the freezing out portion of the tube. This may have been caused by the components falling back down over the column, condensation problems in the unheated portion of the column or by short-circuiting the freezing out caused by poor seals. In order to alleviate these problems, the side wall of the GC was removed and the dewar butted up next to the oven. The condensation tubes could then be inserted right into the oven and the seals could be observed by opening the oven door.

Figure D.1 Preparative GC Tubing Designs

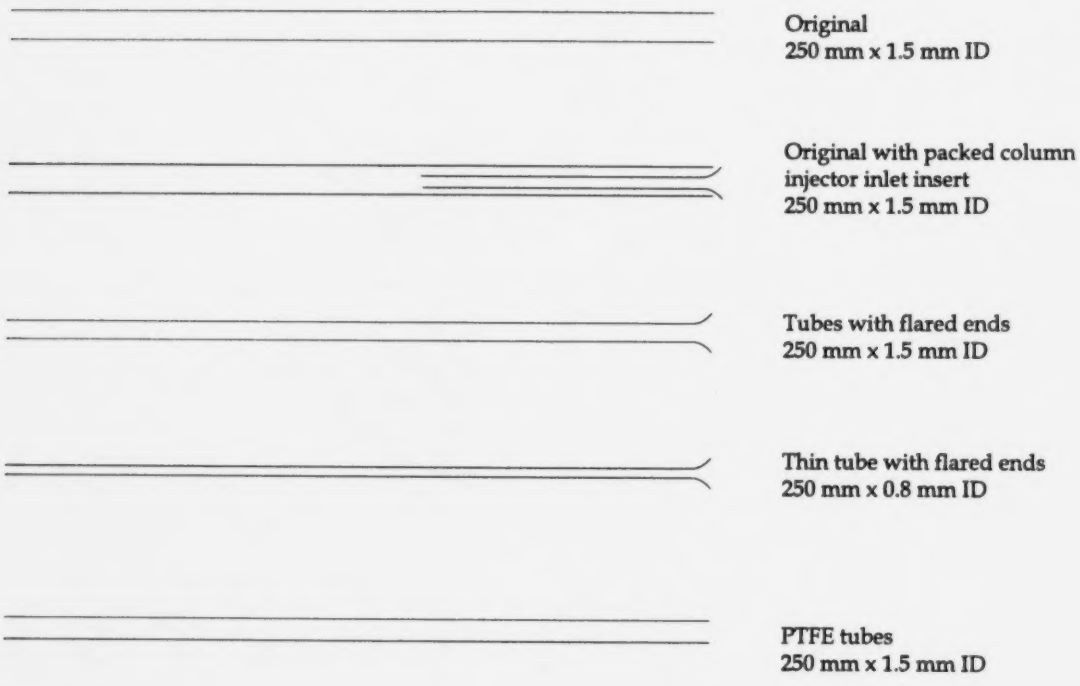

Original
250 mm x 1.5 mm ID
Original with packed column
injector inlet insert
250 mm x 1.5 mm ID
Tubes with flared ends
250 mm x 1.5 mm ID
Thin tube with flared ends
250 mm x 0.8 mm ID
PTFE tubes
250 mm x 1.5 mm ID

Figure D.2 Initial GC Preparative Configuration

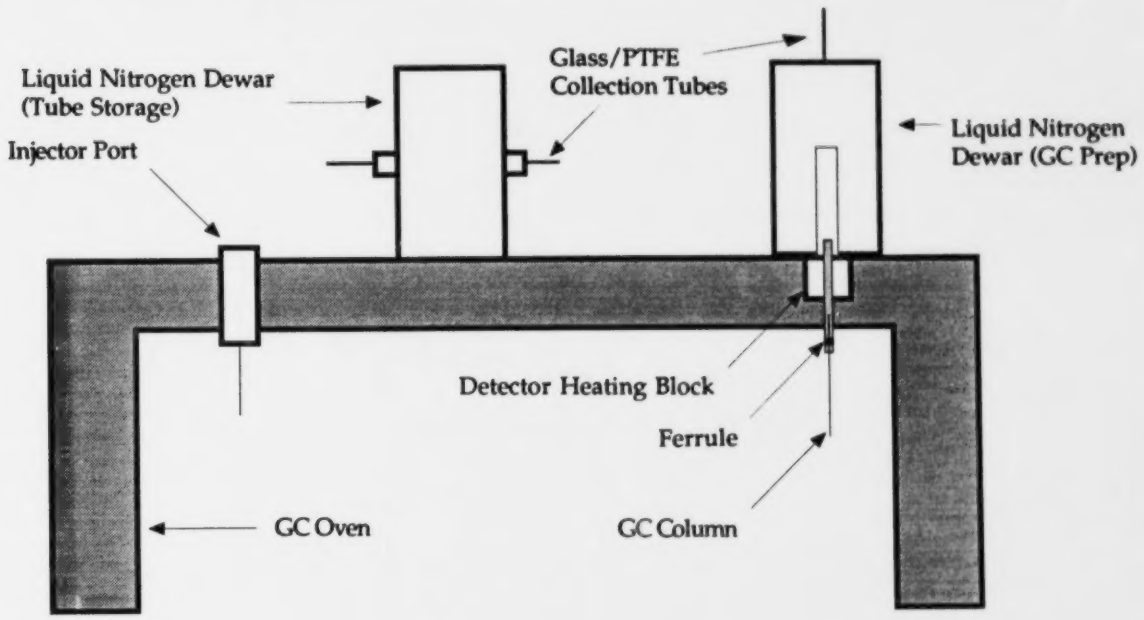
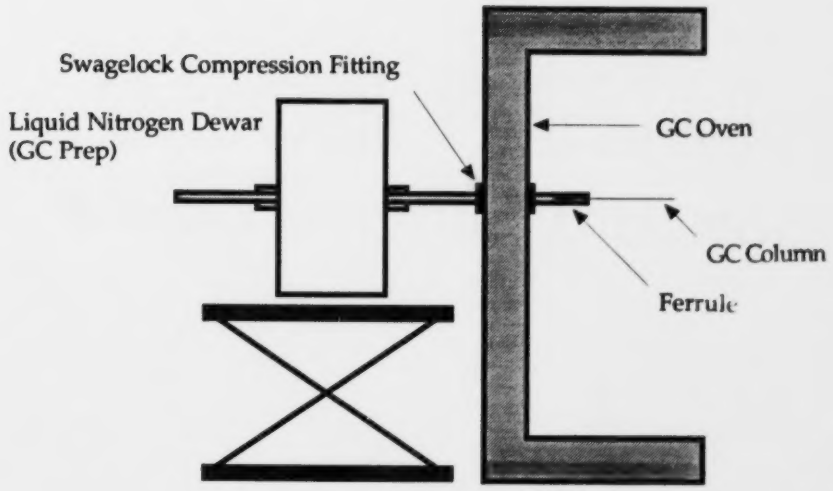


Figure D.3 Second GC Preparative Configuration



Another problem source could have been the condensation tubes themselves and many design changes were made. The initial design was a straight glass tube 20 cm long with an internal diameter of 1.5 mm. The opening at the ends of the tubes tended to be significantly smaller because of fire polishing. Also, with the flat edge, it was hard to obtain an efficient seal and so the next designs either had a flared end or a smaller tube inserted with a flared end. Thinner glass tubing (flared end) with an internal diameter of 0.6 mm was also tried as well as 20 cm x 1.2 mm Teflon® tubes. The Teflon® tubes had the disadvantage of not being straight which caused problems with getting it onto the column and forming a seal. This was especially vexing when rapid tube changes had to be made in order to capture specific fractions of the chromatogram.

Another problem noted was the condensation of water on the outside of the tube when it was placed in the slot in the dewar. It was likely that water was also condensing on the inside of the tube which contributed to the excessive broadening of peaks in the resulting chromatograms.

Preparative GC Discussion

The first attempts at concentrating the odorous compounds obtained in the sniffing work were extremely poor. No recoveries of the compounds of interest were obtained at all. This design was composed of a glass dewar with a tube through it which facilitated the changing of tubes to cut out the desired fractions. The FID was removed and the capillary column was pushed up through the heating block as was done for the sniffing experiments. It was designed this way so as to minimize the modifications to the GC and permit rapid change overs between freeze-concentration and detection by FID. For the first several runs, cuts of the desired fractions were obtained using geosmin and 2-methylisoborneol standards. These cuts were then run on the FID with no response at all. After this the entire chromatogram was frozen out onto a single tube which was then extracted and run on the FID with the same results. At this time several possible explanations were developed. First, the capillary column was vertical in the freezing out tube and it was thought that the compounds were not being eluted as the last few centimeters of the column were kept so cold that the compounds of interest were essentially stopped in that portion of the column. To prevent this, the

stainless steel tube used to transmit heat up from the heating block was replaced with a longer one and the tip of the column lowered so that the entire column was heated. Several more runs were attempted with no recoveries. The column was then moved up and down inside the cold region with similar results.

Originally the seal between the inside of the collection tube and the outside of the capillary column was composed of a Vespel ferrule. These ferrules are used to connect the capillary column to the injector and detector ports. When heated they are slightly malleable and it was thought this would be enough to form the seal. It was also thought that the flow of gas from the capillary column would be sufficient to move the compounds from the column to the wall of the tube. However, gas may have escaped through this imperfect seal. To correct this, PTFE tape was applied to the top of the capillary column forming a tapered cone that would provide a better seal as the tape was very malleable, especially so when heated. However, zero recoveries were again obtained.

It was then proposed that after the compounds were eluted, they fell back over onto the column where they condensed and were not collected when the tubes were extracted. To alleviate this problem the side of the GC was removed, the plug for the MSD pushed through and a hole for the tubing was made through the insulation. The outer tube was attached to the wall of the GC with a double male swagelock connector and compression washers. This held the tube horizontal so that when the collection tube was inserted the compounds would be collected on the bottom of the tube. The design was such that the collection tube could be inserted right though the wall of the GC and into the oven. This was done to prevent any condensation of the compounds on the inside of the capillary column. In order to determine if the compounds were coming through the capillary column as it passed through the wall, 2 µL of geosmin standard was injected and the effluent of the capillary column was sniffed. The earthy musty smell, characteristic of geosmin, was noted at the correct retention time. For the next runs the entire chromatographic run was collected on one tube and then extracted and run on the FID. Low recoveries (<20%) were obtained after several modifications to the seal on the inside of the GC.

Hunt (1967) and Sandra et al. (1980) noted that some compounds form fogs or aerosols when they condense which may not be collected on the sides

of the walls. They suggested a more tortuous path may improve recoveries. Due to the size limitations of the glass dewar, a truly tortuous path was not attempted. However, the internal diameter of the tubes may have been too large and the fog/aerosol may have passed directly through the tube. Smaller tubes were then prepared with flared ends to facilitate changes. Once again only low recoveries similar to the previous experiments were obtained.

Another possible reason for the low/zero recoveries could have been the condensation of water on the tubes that could cause two major problems. First, the water could prevent the deposition of the selected fractions on the tube containing the solvent and secondly it could prevent the separation of the subsequent extract as the volume of water broadens the resulting peaks so that no quantitation is possible. Several of the FID chromatographs of the isolated fractions showed such broadening. Condensation was seen immediately on the outside of the tubes which were placed in the dewars and after 10 minutes the 1.5 cm hole through the dewar was coated over with condensation.

The time between collection and FID detection was on the order of hours as the conversion back to FID required the refitting of the column to the detector, stabilizing the detector, readjusting gas flows and heating up of the column to drive off any remaining contaminants in the end of the column. During this period, some of the compounds of interest may have been lost even though the tubes, and therefore the collected material, were extracted into solvent.

Overall, the utility of preparative GC methods given the resources available, was judged to be unworthy of additional effort.